Motion of Gaseous Ions in Strong Electric Fields

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This paper applies the Boltzmann method of gaseous kinetics to the problem of charged particles moving through a gas under the influence of a static, uniform electric field. The particle density is assumed to be vanishing low, and the ion-atom collisions are assumed elastic, but the field is taken to be strong; that is the energy which it imparts to the charges is not assumed negligible in comparison to thermal energy. In Part I, the formal framework of such a theory is built up; the motion in the field is describable by the drift velocity concept, and the smoothing out of density variations as an anisotropic diffusion process. In Part II, the "high field" case is treated in detail; this is the case, for which thermal motion of the gas molecules is negligible; the equation is solved completely for the case that the mean free time between collisions may be treated as independent of speed; complete solutions are also presented for extreme mass ratios of the ions and the molecules; special attention is given to the case of equal masses, which has to be handled by numerical methods. In Part III, information about the "intermediate field" case is collected; with the help of a convolution theorem the case of constant mean free time is solved; beyond this, only the case of small ion mass (electrons) is available. In Part IV, the diffusion process, whose existence was proved in Part I, is pushed through to numerical results. Part V discusses the scope of the results achieved and demonstrates the possibility of extending them semiquantitatively beyond their original range.

Part I — General Theory of Strong Field Motion

1A. Qualitative Discussion

It is well known that if we consider a mixture of gases under no external forces the steady velocity distribution which establishes itself in the mixture does not depend on the interactions between the gas molecules; we have always a Maxwellian distribution for each species

with a temperature common to all. This result arises from statistical mechanics; the derivation of it is simple and requires few assumptions, yet it enjoys a wide degree of generality. As soon, however, as a non-equilibrium feature is imposed upon the system this simplicity vanishes, and the subject acquires ramifications. Results must now be derived by kinetic theory. The amount of labor required increases, while, at the same time, the result achieved becomes less general.

A mixture of charged particles (ions or electrons; in the following often simply referred to as ions) and gas molecules can in principle never be in equilibrium since the presence of the former in itself represents an instability. However, one might expect, that equilibrium exists in a restricted sense, for instance, as regards motion. Even this is rarely the case under actual conditions of observation. The non-equilibrium features of greatest importance for analyzing ion motion are a constant force (electric field) acting upon one species but not the other (mobility theory), and a concentration gradient for one particular species (diffusion theory). It is the purpose of this paper to apply kinetic theory to these problems, and to compute with its help the most important properties which such a gas of charged particles possesses. The work will be distinguished from similar ones in that the electric field will not be supposed weak; velocity distributions which have no resemblance to the Maxwellian distribution will thus make their appearance. Furthermore, the mass of the charged particles will not be assumed small, which means the possibility of getting results for gaseous ions as well as electrons. Magnetic fields, plasma and A.C. phenomena will, however, be excluded. The quantities of interest under those conditions are the drift velocity of the ions, their energy, energy partition and diffusion constants. These quantities will be calculated by assuming plausible mechanical models. The work just outlined has been published in part in abbreviated form in the Physical Review;[1] the exposition to follow will, however, proceed independently from these articles.

Much of the work which concerns itself with transport processes in gases makes use of perturbation theory. This method permits us to predict the behavior of a gaseous assembly under an electric field or a concentration gradient in the limit when the field or the gradient are vanishingly small. The result of so perturbing a Maxwellian distribution can be expressed through certain constants, such as the mobility or the diffusion coefficient, which involve the Maxwellian distribution *and* the internal interactions, but not the perturbation itself.

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[1] Wannier, G. H., Phys. Rev., **83**, p. 281, 1951 and Phys. Rev., **87**, p. 795, 1952.

The limits of such a procedure can easily be estimated. In the case of an electric field, perturbation techniques apply if the kinetic energy acquired by the ion from the field is small compared to thermal energy. This means at least that the energy acquired in one mean free path be small, i.e.,

$$eE\lambda \ll kT$$

where e is the electronic charge, E the electric field, k Boltzmann's constant, T the absolute temperature, and λ the mean free path. Actually the situation is not even that favorable. If the mass of the ions and the molecules is very different, the energy transferred upon collision is small, and hence the ions possess the ability to store the acquired energy through many collisions; for this reason, the inequality reads more properly

$$\left(\frac{M}{m}+\frac{m}{M}\right) eE\lambda \ll kT,$$

where m is the mass of the ions and M the mass of the gas molecules. After some substitutions this estimate becomes

$$\left(\frac{M}{m}+\frac{m}{M}\right) eE \ll p\sigma, \tag{1}$$

where p is the true gas pressure and σ the collision cross-section. Taking as an example an ion travelling in the parent gas we find

$$\frac{E}{p} \ll 2\,\frac{\sigma}{e} \sim 2\cdot\frac{4\pi\cdot 10^{-16}}{5\cdot 10^{-10}} = 5\cdot 10^{-6} \text{ e.s.u.}$$

or in commonly employed units

$$\frac{E}{p} \ll 2 \text{ volt/cm (mm Hg)}.$$

It is clear that this limit is often surpassed in experimental situations.

The cases in which the limit (1) is applicable are of no further interest here because they are well covered in the literature.[2] A field will be called "low" when it satisfies the criterion (1) and "high" when the inequality is reversed. It is important to notice that a fixed field at a fixed gas density may shift from "low" to "high" through a drop in temperature.

All calculations to follow will contain the assumption of "low ion concentration" which is often made in studies of this sort. It means that

[2] See for instance: A. M. Tyndall, *The Mobility of Positive Ions in Gases*, Cambridge University Press, 1938, Chapter IV.

all effects which ions exert upon each other are neglected. The equation for the distribution function of ionic velocities is then linear instead of quadratic. It is clear that this simplification presents great advantages from the point of view of calculation.

In deriving a criterion for the validity of this assumption we must distinguish two types of effects of the ions upon each other. The first is the space charge effect. In this effect the ions at large distances make the major contribution. Its magnitude depends on apparatus dimensions. The criterion for no space charge distortion of the field E is

$$n \ll \frac{E}{4\pi e X} \tag{2}$$

where n is the number density of the ions and X a suitable length chosen from apparatus dimensions. Inequality (2) is quite stringent because it predicts field distortions at values of n of the order of 10^8 cm^{-3}. This is the value at which it will become impossible, or at least difficult, to make significant experimental measurements. But from the point of view of theory this criterion is not relevant. Space charge does not change the character of the velocity distribution of the ions because the type of ion-ion interaction producing the space charge field is long range and creates only a smooth modification of the electric field which we may presume to have been included in the original field. What we are concerned with here are ion-ion interactions which have a random character and thus are apt to upset a velocity distribution derived from the "low concentration" theory. From this point of view neighboring ions are most effective because their relative location fluctuates rapidly, and hence, the Coulomb force between them will induce mutual scattering. The magnitude of this force is of the order $e^2n^{2/3}$ where n is the number density of the ions. It is known from theory[3] that the effect of a Coulomb force is preferably not represented by discrete "collisons" but hy a continuous bending of the entire path. Thus we come to the conclusion that random ion-ion forces have no effect if the force given above cannot produce a significant deflection in one mean free path. This means

$$e^2n^{2/3}\lambda \ll \text{mean ion energy} \tag{3}$$

According to whether we are in the high or low field region we get different criteria from this. At low field the thermal energy predominates and we get

$$e^2n^{2/3} \ll p\sigma \tag{3a}$$

[3] Mott and Massey, *The Theory of Atomic Collision*, Oxford Press 1933, Chapter III.

At high field the "field" energy predominates and we get

$$e^2 n^{2/3} \ll eE\left(\frac{M}{m} + \frac{m}{M}\right) \tag{3h}$$

A rough evaluation of inequality (3a) for one mm Hg pressure gives

$$n^{2/3} \ll \frac{10^3 \cdot 4\pi \cdot 10^{-16}}{25 \cdot 10^{-20}} = \tfrac{1}{2} \cdot 10^7 \text{ cm}^{-2}$$

$$n \ll 10^{10} \text{ particles/cm}^3$$

This corresponds to a current of about 10^{15} particles/cm^2 sec or 200 μamps/cm^2. At lower pressure the criterion becomes more stringent. Equation (3h) gives similar results.

It is appropriate to survey at this point the past theoretical work treating the "low concentration" theory of ionic motion for arbitrary fields. A rather complete body of work exists for electrons where the following three assumptions seem appropriate: (a) that the mass of an "ion" is very small compared to the mass of a molecule, (b) that the total kinetic energy is conserved in each encounter, and (c) that the angular distribution is isotropic in the center of mass system.

These three assumptions lead to a distribution law given by Chapman and Cowling.[4] The law has considerable flexibility because it permits the substitution of an arbitrary relationship connecting mean free path and speed of encounter. In addition it contains no assumption as to whether we have low or high field. A more specialized and explicit distribution law is obtained if we assume in addition: (d) that the collision cross-section is independent of the speed of encounter (hard sphere approximation); and (e) that we deal with the high field case only. The special law resulting in this case is the distribution law of Druyvesteyn.

If an improvement over the Chapman-Cowling distribution for electrons is desired account should be taken of inelastic collisions, that is assumption (b) should be discarded. Work in that direction has been carried out by Smit, Allen[5] and others.

The assumption to be discarded first in theory of ionic motion is, of course, assumption (a). In order to understand what this implies we must understand what advantages assumption (a) has in a calculation. In the limit when the ionic mass is very small the encounters with gas

[4] Chapman-Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press 1939, Sections 18.7–18.74. Other references are found there.

[5] Smit, J. A., Physica, **3**, p. 543, 1937 and H. W. Allen, Phys. Rev., **50**, p. 707, 1937.

molecules become such that momentum is lost quickly, but energy is accumulated in the form of random motion. As a result of this we end up with a distribution function which is very nearly spherically symmetrical in velocity space. Such a situation permits obvious procedures through which the entire calculation is simplified. These procedures will not longer be available when assumption (a) is dropped.

Knowledge concerning the structure of the velocity distribution function for gaseous ions is practically nonexistent at this time. Hershey, who deals with the motion of ions in the high field case, simply substitutes for it a Maxwellian distribution with an unknown offset of the origin and unknown temperature parameter,[6] shown in Fig. 1(a). He then computes these two parameters by applying the laws of conservation of momentum and kinetic energy. It is to be expected that this procedure should give reasonable values for the mobility and the mean energy of the ion; indeed, if we consider the polarization force only, we get *exactly* the right values; the reason for this is that one may evaluate velocity averages for inverse fifth power forces ignoring the distribution function[7] and that he did this in effect for the drift velocity and the

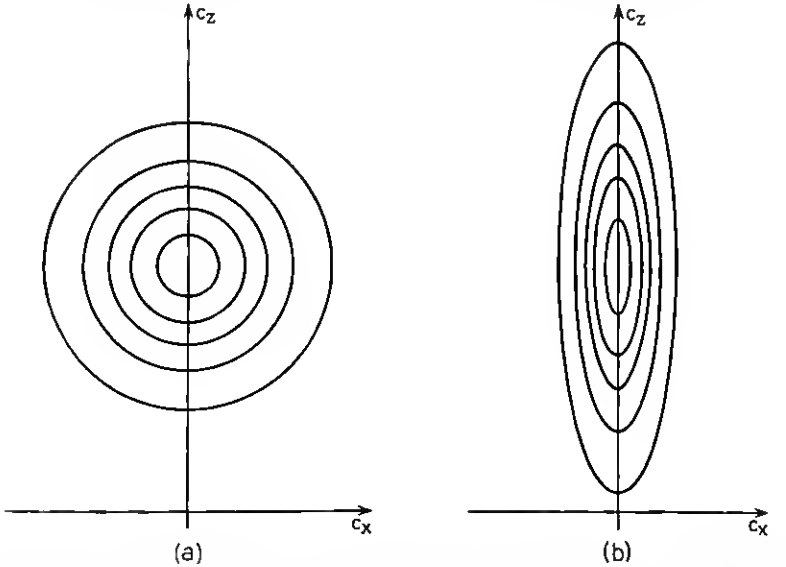

Fig. 1 — Simplified pictures for the high field velocity distribution of gaseous ions. (a) Hershey's assumption. (b) Modification with correct second moments.

[6] Hershey, A. V., Phys. Rev., **56**, p. 916, 1939.

[7] This will be shown in Section IIB.

total energy. In order to test whether an offset Maxwellian distribution is a satisfactory approximation we have to go one step furtber and examine the partition of tbe energy among the three degrees of freedom. There we find Hershey's distribution in error, for he assumes equipartition for the random motion, while, in reality, the random energy parallel to the field is much higber than at right angles,[7] giving the distribution a decided "ridge" structure. Tbis discrepancy could be taken into account by the use of an elliptically distorted Maxwellian distribution, shown in Fig. 1(b), and tbis may prove to be convenient in some applications.

For a detailed knowledge of the distribution function it is necessary to specify the interaction between an ion and a molecule. This interaction can be, broadly speaking, summarized under three headings: (a) the polarization force, (b) the sbort distance repulsion, and (c) symmetry effects. The polarization force arises because an ion, when passing close to a molecule, induces on it a dipole moment; this moment is then attracted by the charge of the ion. The attractive force F resulting from this is

$$F = \frac{2e^2P}{\rho^5} \tag{4}$$

where P is the polarizability of a gas molecule and e the charge of the ion. The force varies inversely as the fiftb power of the distance ρ; for such a force the cross section σ varies inversely as the speed of encounter γ. Whenever the cross section shows this type of variation it is advantageous to define a mean free time τ rather than a mean free path λ. The formula is

$$\tau = \frac{1}{N\sigma\gamma} \tag{5}$$

There is a standard difficulty which arises when one tries to make use of a formula of the type (5). For most force laws, a total cross-section σ cannot be defined; a differential cross section per unit solid angle always exists, but it becomes infinite in the forward direction because of small deflections suffered by particles passing by each other at a large distance. Thus equation (5) is, strictly speaking, meaningless. This is actually never a difficulty in the computation of a physical quantity. However, equation (5) is convenient for order-of-magnitude thinking and the question arises how it can be reasonably interpreted. The general method of salvaging (5) — excluding a small forward cone from consideration — is of little value for tbis purpose. An analysis of tbe inverse fourth power

attractive potential shows a hetter way out. The potential gives rise to two kinds of orhits; orhits of large angular momentum which look somewhat like hyperholas, shown in Fig. 2(a), and orhits of small angular momentum for which the particles are "sucked" toward each other in a spiralling movement until a repulsive force reverses the trend, as shown in Fig. 2(h).[8] A calculation of Hassé[9] shows that the latter type of motion is much more efficient in scattering than the former and one gets therefor a picture which is semiquantitatively correct if one substitutes into (5) the cross-section for spiralling collisions and assumes isotropic scattering.[10] This cross section equals

$$\sigma = 2\pi \sqrt{\frac{1}{m} + \frac{1}{M}} \frac{\sqrt{P}\, e}{\gamma} \tag{6}$$

A numerical estimate of the cross section (6) automatically leads one to compare it with the short distance repulsion familiar from the kinetic theory of gases. The two are of the same order, but for the usual gaseous speeds (which enter into (6) through γ) and small molecules the cross

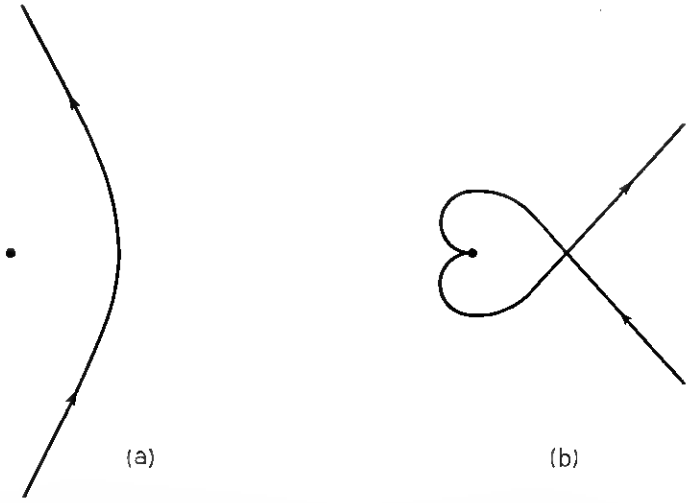

Fig. 2 — Sample orbits (schematic) showing the motion of a particle in the polarization force field. (a) Hyperholic orhit (large angular momentum). (b) Spiralling orhit (small angular momentum).

[8] There are quantum mechanical analogues to these classical ideas; they should lead to practically identical answers unless the angular momentum quantum number is small.

[9] Hassé, H. R., Phil. Mag., **1**, p. 139, 1926.

[10] This will he discussed more fully in Section IIIB.

section (6) is bigger. This situation is accentuated in an actual scattering calculation which shows an attractive force to be generally more efficient than a repulsive force of equal range.

A detailed numerical discussion of these questions is found in Massey and Mohr[11] for the case of He^+ ions moving through He gas. Their interest is in the low field mohility. They show that for this problem the repulsive force makes so little difference that it could be neglected entirely without much affecting the results. It does finally come out that the polarization force gives a mobility which is too big by a factor of two. But the additional scattering is due to an effect which we listed above under (c): namely a resonance attraction between the He atom and the He^+ ion for which the cross section is abnormally large. It should he possible to eliminate this effect by increasing the cross section (6) until it masks even this special effect. Lowering the field is not sufficient to achieve this because of the temperature motion; it would he necessary in addition to reduce the absolute temperature hy a sizeable factor and so to decrease the value of γ in (6). Thus we are led to the prediction that if the temperature of He is reduced the mohility of He^+ ions in He should gradually rise from its "anomalous" value of 12 cm^2/volt sec to the "normal" value of 22 cm^2/volt sec, which one gets by taking account of polarization forces only.

IB. GLOSSARY

The complicated appearance of equations in gaseous kinetics suggests special care in the use of symbols and a convenient arrangement for the reader to find their meaning. It is hoped that the glossary to follow will accomplish this purpose. It explains all symbols except those used at one location only.

Generally, Latin capital letters will refer to the gas molecules and Latin lower case letters to the ions; Greek letters will have no special relationship; exceptions will be made for generally recognized symbols. Thus we define

E, $\mathbf{E}$ = electric field.
x, y = cartesian coordinates at right angles to the field direction.
z = cartesian coordinate along the field direction.
$\mathbf{r}$ = position vector with components x, y, z.
t = time.
m = ionic mass.
e = ionic charge.

[11] Massey, H. S. W., C. B. O. Mohr, Proc. Roy. Soc., **144A**, p. 554, 1931.

a, $\mathbf{a} = \dfrac{e\mathbf{E}}{m}$ = ionic acceleration.

b = impact parameter.

b_{lim} = limiting value of the impact parameter separating hyperbolic and spiralling orbits (equation (125)).

c, $\mathbf{c}$, $\mathbf{c}'$, c_x, c_f, c_i = various ionic velocities or components.

e_x, e_y, e_z = energies of ionic motion (or "high field" parts thereof) along x, y, z.

e_z^* = random part of the above energy,

$\mathbf{j}_t$ = total particle current density of the ions (may be a function of $\mathbf{r}$ and t).

$\mathbf{j}$ = partial current density induced by the concentration gradient; see equation (22).

k = Boltzmann's constant (only when followed directly by T).

k, $\mathbf{k}$ = relative concentration gradient of the ions (a different use is made of k in Section IIE).

n = number density of the ions (may be a function of $\mathbf{r}$ and t).

p, q, r, s = undetermined constants; used three times independently (equations (82), (90) and (160)).

$p^{(0)}$, $p^{(1)}$ = various approximations to these numbers.

$\mathbf{u}$, $\mathbf{u}'$, $\mathbf{v}$ = ionic velocities.

$\mathbf{w}$ = ionic velocity rendered dimensionless (see eq. (75) or (85)).

$\mathcal{I}$ = the inner integral in the double integral eq. (69).

$\mathbf{C}$, $\mathbf{C}'$ = molecular velocities.

$\mathfrak{D}$ = ionic diffusion tensor.

$D_{||}$, $D_{\perp}$ = components of above tensor parallel and perpendicular to the field.

M = molecular mass.

N = number density of the molecules.

P = molecular polarizability.

T = gas temperature.

$\mathbf{U}$, $\mathbf{U}'$ = molecular velocities.

X, Y = left and right hand sides of equation (111a).

$\beta = \dfrac{1}{2kT}$ = temperature parameter (A different use of β is made in Section IIIB where it is the relative impact parameter b/b_{lim}).

γ, γ', η, η' = relative velocities of ion and molecule.

ξ, η, ζ = cartesian coordinates oriented on $\mathbf{c}$.

ρ = distance between ion and molecule.

σ = collision cross section of ions and molecules (may be a function of γ).

$\lambda = \dfrac{1}{N\sigma}$ = mean free path of ion between collisions with molecules (may be a function of γ).

$\tau = \dfrac{1}{N\sigma\gamma}$ = mean free time for the ion between collisions witb molecules.

τ_s = same parameter for "spiralling" collisions.

$\alpha = \dfrac{d\ell n\tau(\gamma)}{d\ell n\gamma} + 1$. It is assumed constant in Section ID.

χ, χ_o, χ_u = angle of scattering of ion and molecule in the center of mass system.

κ = angle of scattering of the ion by a molecule in tbe laboratory system.

ϵ = scattering azimuth of ion and molecule in the center of mass system.

ω = scattering azimuth in the laboratory system (azimuth of the initial ion velocity about the final ion velocity).

ϑ, ϑ' = angle between velocity vector and field direction.

ψ, φ, θ, ϕ, δ = other angles (these angles are defined on spherical triangles which are exhibited in Figs. 8 and 15.

$d(\mathbf{c}, \mathbf{r}, t)$ = density function of ions in phase space.

$m(\mathbf{c}) = \left(\dfrac{\beta m}{\pi}\right)^{3/2} \exp(-\beta mc^2)$ = Maxwellian velocity distribution function for ionic mass.

$M(\mathbf{C}) = \left(\dfrac{\beta M}{\pi}\right)^{3/2} \exp(-\beta MC^2)$ = Maxwellian velocity distribution function for molecular mass.

$h(\mathbf{c})$ = "high field" distribution function of the ions for the case that the spatial distribution is uniform (the exact meaning of this term is to be explained in the text).

$f(\mathbf{c})$ = true velocity distribution of the ions for the case tbat tbe spatial distribution is uniform.

$g(\mathbf{c})$ = correction to $f(\mathbf{c})$ or $h(\mathbf{c})$ for the case of a constant relative concentration gradient $\mathbf{k}$.

$\delta(\mathbf{c})$ = vectorial δ-function in velocity space.

$Ei(x) = \displaystyle\int_x^\infty \frac{e^{-\xi}}{\xi}\, d\xi$ (suppression of two minus signs).

$I_0(x)$ = modified Bessel function of order 0.

$K_0(x)$, $K_1(x)$ = Modified Hankel functions of order 0, 1. (Alteration of Macdonald function by a factor $\dfrac{2}{\pi}$).

$P_\nu(x)$ = Legendre Polynomials.

$h_\nu(c)$, $g_\nu(c)$ = expansion coefficients which result when $h(\mathbf{c})$, $g(\mathbf{c})$ are expanded in Legendre Polynomials about the field direction.
$I_{s,\nu}(\chi)$ = A set of functions of the scattering angle defined in (48).
$\langle \quad \rangle$ = the quantity in pointed brackets is to be averaged.
$\langle s, \nu \rangle$ = abbreviation for $\langle w^s P_\nu (\cos \vartheta) \rangle$; the average is taken over $h(\mathbf{w})$.
$\{s, \nu\}$ = A normalized correction to $\langle s, \nu \rangle$ contributed by $g(\mathbf{w})$; see equation (155).

A special convention will be adopted to distinguish velocities before and after a collision:

$\mathbf{c}', \mathbf{C}'$ = velocities before the collision.

$\mathbf{c}, \mathbf{C}$ = velocities after the collision.

When used in this fashion the twelve components of the four vectors above satisfy the four identities:

$$m\mathbf{c}' + M\mathbf{C}' = m\mathbf{c} + M\mathbf{C} \tag{7}$$

$$mc'^2 + MC'^2 = mc^2 + MC^2 \tag{8}$$

The same convention is to apply to other vector quadruples, such as

$$\mathbf{u}, \mathbf{U}, \mathbf{u}', \mathbf{U}'$$

For the velocities in the center of mass system we use

$\boldsymbol{\gamma}' = \mathbf{c}' - \mathbf{C}'$ = relative velocity before the collision.

$\boldsymbol{\gamma} = \mathbf{c} - \mathbf{C}$ = relative velocity after the collision.

In consequence of (7) and (8) the γ's obey the relation

$$\gamma'^2 = \gamma^2 \tag{9}$$

The multiple integrations occurring in the theory are of the following two types. Either they are over the three components of a velocity in a Cartesian velocity space; we shall denote such integrations by $d\mathbf{c}$, $d\mathbf{u}$, $d\mathbf{U}'$, etc. Or they are proper "collision" integrations which classically have the form

$$\gamma\, b\, db\, d\epsilon$$

where b is an impact parameter and ϵ an azimuth. In most cases these integrals depend on extraneous factors for their convergence but this fact is usually disregarded for convenience; we shall follow this habit by

writing the above differential in the form

$$\frac{1}{4\pi}\gamma\sigma(\gamma)\Pi(\chi)\sin\chi\,d\chi\,d\epsilon = \frac{1}{4\pi}\gamma\sigma(\gamma)\Pi(\chi)\,d\Omega_\gamma$$

Here $d\Omega$ is meant to represent an integration over a solid angle and the subscript γ, that it is over the solid angle swept out by the vector $\boldsymbol{\gamma}$. The notation makes use of the fact that the choice of the polar axis is arbitrary in such an integration. The function $\Pi(\chi)$ is the probability of scattering which equals unity for isotropic scattering. In cases where small angle scattering is infinitely probable the above expression becomes meaningless, strictly speaking, $\Pi(\chi)$ being a δ-function at $\chi = 0$ and σ being infinite. However if a quantity such as $1 - \cos\chi$ is multiplied in, which removes the δ-function then the integration gives a finite number which may be denoted by $\langle\sigma\cdot(1 - \cos\chi)\rangle$.

IC. FORMAL SURVEY OF THE THEORY

Under the assumptions stated in Part IA we may describe the motion of ions in a gas by their density in phase space. The change in time of this function is described by a Boltzmann equation[12] which, in our notation, reads

$$\frac{\partial d(\mathbf{c},\mathbf{r},t)}{\partial t} + \mathbf{a}\cdot\frac{\partial d(\mathbf{c},\mathbf{r},t)}{\partial \mathbf{c}} + \mathbf{c}\cdot\frac{\partial d(\mathbf{c},\mathbf{r},t)}{\partial \mathbf{r}} = \frac{N}{4\pi}\iint\{M(\mathbf{C}')d(\mathbf{c},\mathbf{r},t) - M(\mathbf{C})d(\mathbf{c},\mathbf{r},t)\}\gamma\sigma(\gamma)\Pi(\chi)\,d\Omega_\gamma\,d\mathbf{C} \tag{10}$$

The equation is linear in the unknown function $d(\mathbf{c},\mathbf{r},t)$; this is due to neglect of ion-ion collisions, as stated earlier. The negative term on the right hand side actually reduces to a known function of $\mathbf{c}$ multiplying $d(\mathbf{c},\mathbf{r},t)$. The positive term is a genuine integral term; it has been shown by Pidduck[13] that the number of integrations in it can be brought down from five to three; this reduction will not be made use of in the following.

If there were no terms on the left hand side of equation (10) then the solution of it would have the equilibrium form

$$d(\mathbf{c},\mathbf{r},t) = nm(\mathbf{c}) \tag{11}$$

where n is a constant. This result is a direct consequence of equation (8) which makes the curly bracket in (10) vanish identically when Maxwellian functions are inserted.

[12] See Reference 4.

[13] Pidduck, F. B., Proc. Lond. Math. Soc., **15**, p. 89, 1915.

The function $m(\mathbf{c})$ is not the solution of our problem because of the presence of the second and third term on the left which arise from an electric field and a density variation respectively. These disturbances will be assumed of different relative importance. The density variation will be assumed sufficiently small so that the third term can be treated by perturbation theory; the field term, on the other hand will be taken so large that the equilibrium distribution (11) no longer represents a first approximation to the solution. In consequence, the equation is solved in two stages. In the first, only the second term on the left is retained, and the resultant equation is treated rigorously; in the second, the full equation (10) is used, but the new terms are taken as perturbations.

The first stage describes those properties of the ion gas which it possesses when assumed of uniform density. Since the field is also assumed uniform and not changing in time, the dependence on $\mathbf{r}$ and t drops out. We may then write

$$d(\mathbf{c}, \mathbf{r}, t) = nf(\mathbf{c}) \tag{12}$$

where n is a constant and $f(\mathbf{c})$ is a velocity distribution function. The equation for f reads

$$\mathbf{a}\cdot\frac{\partial f}{\partial \mathbf{c}} = \frac{N}{4\pi}\iint \{M(\mathbf{C}')f(\mathbf{c}') - M(\mathbf{C})f(\mathbf{c})\}\gamma\sigma(\gamma)\Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} \tag{13}$$

with the side condition

$$\int f(\mathbf{c})d\mathbf{c} = 1 \tag{14}$$

As a result of solving (13) we shall obtain the distribution function $f(\mathbf{c})$ as a function of the electric field contained in a. This distribution differs essentially from the Maxwellian one in that it is not symmetric about the origin. The vectorial mean of the velocity is therefore not zero

$$\langle \mathbf{c} \rangle = \int f(\mathbf{c})\mathbf{c}\, d\mathbf{c} \neq 0 \tag{15}$$

This is the drift velocity of the ion in the field which is reached as a compromise between the acceleration $\mathbf{a}$ and the frictional losses caused by the ion-atom collisions. From the structure of equation (13) there is one general prediction that can be made concerning this velocity, namely that it depends on the gas density and the field only through a/N; this is the well known E/p_0 of the experimental analysis. This type of

dependence does not only hold for $\langle \mathbf{c} \rangle$, but for all averages derivable from $f(\mathbf{c})$, notably tho mean energy.

A more important formal prediction can be made about the second stage of the contemplated calculation. For it will be shown now that the diffusion concept is still applicable in the presence of a strong electric field. It is true, that if we have a variable density in space the primary motion observed is not diffusive but a displacement of the entire density pattern with the drift velocity $\langle \mathbf{c} \rangle$. However, once this dominant component is subtracted out, then a supplementary current proportional to the density gradient is identified. The constant of proportionality is anisotropic, that is, we have a diffusion tensor rather than a diffusion coefficient. The tensor is axially symmetric about the field direction, yielding a longitudinal and a transverse diffusion coefficient.

To demonstrate these features it is convenient to assume a special type of variation of ion density in space. As we shall see the velocity distribution is primarily sensitive to the relative density gradient $\mathbf{k}$; we shall therefore assume it to be a constant. In other words we set

$$n(\mathbf{r}, t) = n_0 \exp [\mathbf{k} \cdot (\mathbf{r} - \langle \mathbf{c} \rangle t)] \tag{16}$$

The relation can of course not hold everywhere since n increases beyond all bounds in one direction, but we must remember here that we are doing perturbation theory, that is $\mathbf{k}$ is assumed small. The inconsistencies in the assumption (16) can then be pushed as far away as we please. Furthermore there is no inconsistency at all in the half space where n decreases. It is to be observed that according to the assumption (16) the spatial distribution is moving unchanged through space with the drift velocity $\langle \mathbf{c} \rangle$. This seems to contradict the program of finding tbe effect of diffusion upon $n(\mathbf{r}, t)$. However, we follow in tbis simply conventional steady state computational methods in whicb a gradient is assumed maintained from an infinitely strong source; tbe modification appears then as a change in the velocity distribution function, which, in turn, yields a steady diffusion current. We set therefore

$$d(\mathbf{c}, \mathbf{r}, t) = n(\mathbf{r}, t)[f(\mathbf{c}) + g(\mathbf{c})] \tag{17}$$

where $g(\mathbf{c})$ is a correction to the solution of (13) which arises from the assumption (16). It follows from the definition of $n(\mathbf{r}, t)$ and (14) that

$$\int g(\mathbf{c}) d\mathbf{c} = 0 \tag{18}$$

The consistency of the assumptions (16) and (17) witb equation (10) becomes evident when they are substituted into this equation. We

find, after simplification with (13)

$$\mathbf{a}\cdot\frac{\partial g(\mathbf{c})}{\partial \mathbf{c}} + \frac{N}{4\pi}\iint \{M(\mathbf{C})g(\mathbf{c}) - M(\mathbf{C}')g(\mathbf{c}')\}\gamma\sigma(\gamma)\Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} = -\mathbf{k}\cdot(\mathbf{c} - \langle\mathbf{c}\rangle)\{f(\mathbf{c}) + g(\mathbf{c})\} \tag{19}$$

This is an equation in velocity space only, $\mathbf{r}$ and t having disappeared completely; this justifies the assumptions. In solving the equation we observe that our interest is only in diffusion, that is, the current resulting from a concentration gradient when treated in first order perturbation. In this case both $\mathbf{k}$ and $g(\mathbf{c})$ are to be treated as small and their product in (19) is to be neglected. The equation then becomes

$$\mathbf{a}\cdot\frac{\partial g(\mathbf{c})}{\partial \mathbf{c}} + \frac{N}{4\pi}\iint \{M(\mathbf{C})g(\mathbf{c}) - M(\mathbf{C}')g(\mathbf{c}')\}\gamma\sigma(\gamma)\Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} = -\mathbf{k}\cdot(\mathbf{c} - \langle\mathbf{c}\rangle)f(\mathbf{c}) \tag{20}$$

The homogeneous prototype of this inhomogeneous equation is (13); an arbitrary amount of $f(\mathbf{c})$ could thus be added to a particular solution of (20) were it not for the orthogonality condition (18) which makes the solution definite.

The existence of the diffusion phenomenon follows easily from equation (20). The total current $\mathbf{j}_t$ is given by

$$\mathbf{j}_t(\mathbf{r}, t) = \int d(\mathbf{c}, \mathbf{r}, t)\mathbf{c}\, d\mathbf{c} \tag{21}$$

Upon substitution of (17) into this expression two terms result

$$\mathbf{j}_t(\mathbf{r}, t) = n(\mathbf{r}, t)\langle\mathbf{c}\rangle + \mathbf{j}(\mathbf{r}, t) \tag{22}$$

with

$$\mathbf{j}(\mathbf{r}, t) = n(\mathbf{r}, t)\int g(\mathbf{c})\mathbf{c}\, d\mathbf{c} \tag{23}$$

The first term in (22) is seen from (15) to just equal the product of the density and the drift velocity; this is the expected drift current. The new current $\mathbf{j}(\mathbf{r}, t)$ induced by the density gradient is thus given by (23). From (20) it follows that $g(\mathbf{c})$ is a linear function of the three components k_x, k_y, k_z with coefficients which do not depend on the density or its gradient, but only on the unperturbed velocity distribution $f(\mathbf{c})$; furthermore, the first two of these coefficients are equal. Hence, from (23) $\mathbf{j}$ comes out as a linear function of the three quantities $n(\mathbf{r}, t)\cdot k_x$, $n(\mathbf{r}, t)\cdot k_y$, $n(\mathbf{r}, t)\cdot k_z$; these are the components of the density gradient

as is evident from (16); in addition tbe multipliers of the first two components are equal. We may write therefore

$$\mathbf{j}(\mathbf{r}, t) = -(\mathfrak{D}) \frac{\partial n}{\partial \mathbf{r}} \tag{24}$$

where $(\mathfrak{D})$ is a tensor which is axially symmetric about the field direction; its two components which we shall call the longitudinal diffusion coefficient $D_{||}$ and the transverse coefficient $D_{\perp}$ are computed entirely from the unperturbed velocity distribution $f(\mathbf{c})$. This makes $D_{||}$ and $D_{\perp}$ independent of the density or its gradient; it is to be noted, however, that they do depend on the electric field as a parameter hecause this quantity enters several times in the course of the computation.

ID. DIMENSIONAL ANALYSIS

Dimensional analysis is a convenient tool in a qualitative discussion of (13) and (20). In order to get results the situation has to he schematized somewhat, but not so mucb as to impair its usefulness. In the first place it is convenient to keep in mind the two limiting cases of high and low field, as discussed in the introduction. In addition some assumption must he made ahout $\sigma(\gamma)$ and $\Pi(\chi)$ occurring under the integral sign. The most convenient way to dispose of $\Pi(\chi)$ is to take it as independent of γ. This happens to be true for the two models treated in detail later, the polarization force model, and the bard sphere model. Actually $\Pi(\chi)$ can be taken as approximately independent of γ in a wider sense. The forces which produce scattering are either repulsive or short range attractive, that is, long range attractice forces are ahsent. As long as this is the case the scattering is roughly isotropic and hence can change but little with γ.[14]

A more drastic assumption is needed to dispose of $\sigma(\gamma)$. We must assume

$$\sigma(\gamma) \cdot \gamma^{\alpha} = \Gamma \tag{25}$$

where α and Γ are taken to be constants. Tbis assumption contains two important special cases in it. They arise respectively by taking $\alpha = 0$ and $\alpha = 1$. The case $\alpha = 0$ is the case of a constant mean free path as exemplified by the hard sphere model. The case $\alpha = 1$ is the case of constant mean free time; it is applicable to the polarization force as dis-

[14] This statement is checked in detail in Section IIIB for the polarization force. This is the attractive force with the longest range which can arise in this field.

cussed in Section IA. When (25) is inserted into (13) it is seen that a, N and Γ enter only in the combination $a/N\Gamma$. The quantity

$$\left(\frac{a}{N\Gamma}\right)^{\frac{1}{2-\alpha}}$$

bas the dimension of a velocity. A second such quantity is

$$\left(\frac{kT}{M}\right)^{1/2}$$

which arises from the Maxwellian functions under the integral sign.[15] In the high field case, this quantity does not enter, that is, the velocity distribution functions for the molecules could be replaced by δ-functions at the origin. Hence the first combination controls all velocity averages. For the mean drift velocity, we can thus write

$$\langle c_z \rangle = \text{const} \cdot \left(\frac{a}{N\Gamma}\right)^{\frac{1}{2-\alpha}} \tag{26a}$$

This formula gives the variation of the drift velocity with the electric field. It is worth while writing the result out explicitly for the two special cases discussed above. The first is the case of constant mean free path, $\alpha = 0$, for which

$$\langle c_z \rangle = \text{const} \cdot a^{1/2} \lambda^{1/2} \tag{26b}$$

This is a drift velocity varying as the square root of the field or a mobility varying inversely as tbe square root of the field. The second case is the one of constant mean free time $\alpha = 1$, for which

$$\langle c_z \rangle = \text{const} \cdot a\tau \tag{26c}$$

This means a drift velocity proportional to the field or a constant mobility.

In the low field case we cannot disregard one of the two velocity parameters constructed ahove; hut now equation (13) is to be solved by perturhation theory only, it then yields a drift velocity varying with the first power of $a/N\Gamma$. Dimensional analysis then yields tbe dependence of the mobility on the temperature. We find

$$\langle c_z \rangle = \text{const} \cdot \frac{a}{N\Gamma} \left(\frac{kT}{M}\right)^{\frac{\alpha-1}{2}} \tag{27a}$$

[15] Dimensional analysis is incapable of distinguishing between m and M; this means that we cannot master dependence on mass by the method of this section; all our "pure numbers" are actually unknown functions of m/M.

with the special cases

$$\langle c_z \rangle = \text{const} \cdot a\lambda \left(\frac{kT}{M}\right)^{-1/2} \tag{27b}$$

for constant mean free path and

$$\langle c_z \rangle = \text{const} \cdot a\tau \tag{27c}$$

for constant mean free time. Comparison of (26c) and (27c) might lead one to surmise that we have here twice the same formula. This is indeed the case, as will be shown in Section IIIA.

Proceeding now to the diffusion problem, we observe from (20), (23) and (24) that we must add the quantity

$$\frac{nk}{N\Gamma}$$

to the previous list of parameters when computing the diffusion current. However, the current is always linear in this quantity, which means that the diffusion coefficients contain the factor

$$\frac{1}{N\Gamma}$$

and beyond this factor depend on the same variables as previously. This gives in the high field case

$$D = \text{const} \cdot \frac{1}{N\Gamma} \cdot \left(\frac{a}{N\Gamma}\right)^{\frac{1+\alpha}{2-\alpha}} \tag{28a}$$

with the special cases

$$D = \text{const} \cdot a^{1/2}\lambda^{3/2} \tag{28b}$$

and

$$D = \text{const} \cdot a^2\tau^3 \tag{28c}$$

In the low field case, the diffusion process becomes independent of the field and we get

$$D = \text{const} \cdot \frac{1}{N\Gamma} \left(\frac{kT}{M}\right)^{\frac{1+\alpha}{2}} \tag{29a}$$

with the special formulas

$$D = \text{const} \cdot \lambda \left(\frac{kT}{M}\right)^{1/2} \tag{29b}$$

and

$$D = \text{const} \cdot \tau \frac{kT}{M} \tag{29c}$$

The information in the formulas (29) is now new, but dependent on (27) through a universal relation first discovered by Nernst and derived independently for gases by J. J. Thomson; it is widely known as the Einstein relation. It states that

$$D = \frac{\partial \langle c_z \rangle}{\partial a} \cdot \frac{kT}{m} \tag{30}$$

Equation (30) contains of course more than is obtainable from (27) and (29), since it relates one undetermined constant to another in a known way.

The dimensional methods of this section are convenient for a rough classification of experimental material. Figs. 3 to 7 show the drift velocities

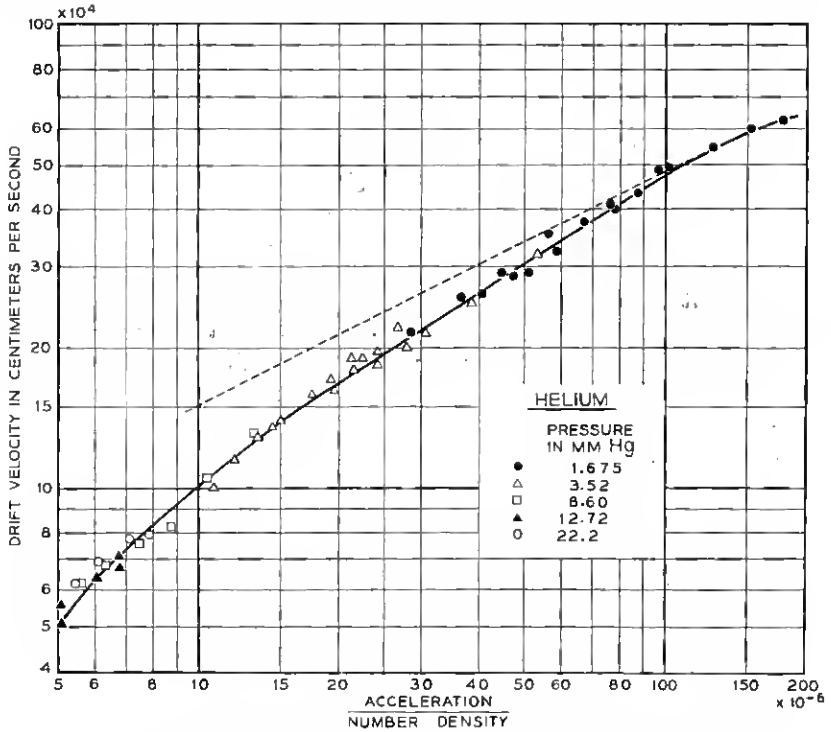

FIG. 3 — Drift velocity in an electric field of He^+ ions in helium gas. Comparison of observed results with an "asymptotic" straight line of slope ½.

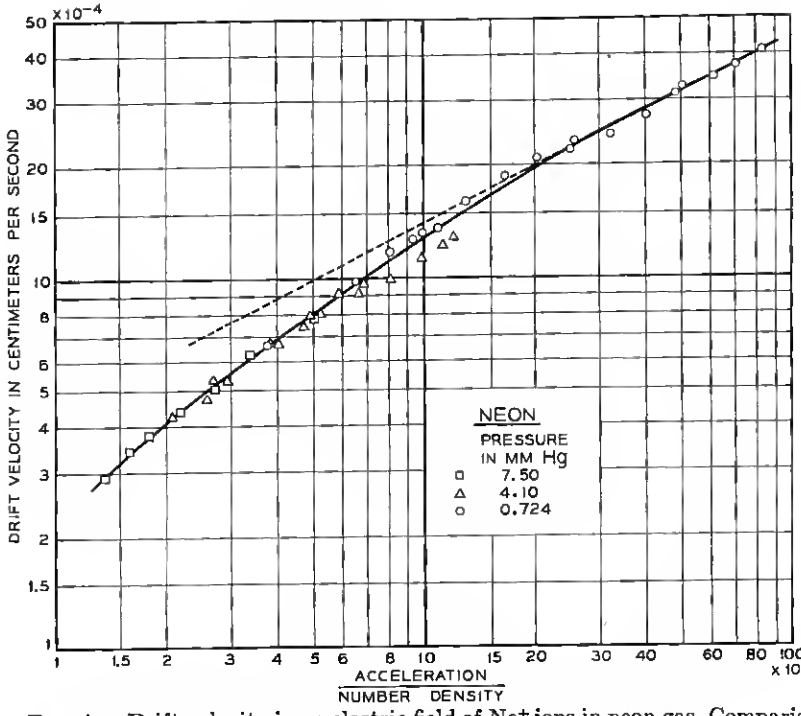

FIG. 4 — Drift velocity in an electric field of Ne^+ ions in neon gas. Comparison of observed results with an "asymptotic" straight line of slope ½

in the parent gas, observed for He^+, Ne^+, A^+, Kr^+ and Xe^+. The plot is a log-log plot of these quantities against a/N, a variety of fields having heen used to determine each point. The data are taken from measurements of J. A. Hornbeck[16, 17] and R. N. Varney.[18] These data verify in the first place that the drift velocity depends on a and N only in the combination a/N. Beyond this we see that the curves consist of two straight line portions: in the lower field portion $\langle c_z \rangle$ is proportional to a/N, in the higher is proportional to $\sqrt{a/N}$. We recognize in this latter region the high field dependence predicted in equation (26h). We learn from this that the collision cross section hetween nohle gas atoms and their ions is approximately constant in the experimentally significant velocity range. To determine these collision cross sections the computation of only a single numher, namely the one entering into

[16] Hornbeck, J. A. and G. H. Wannier., Phys. Rev., **82**, p. 458, 1951.
[17] Hornbeck, J. A., Phys. Rev., **84**, p. 615, 1951.
[18] Varney, R. N., Phys. Rev., **88**, p. 362, 1952.

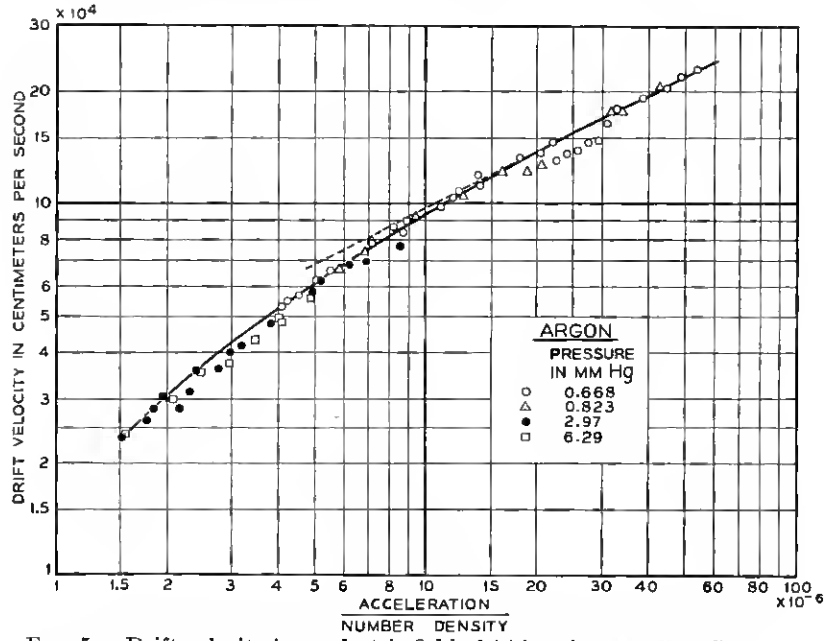

FIG. 5 — Drift velocity in an electric field of A^+ ions in argon gas. Comparison of observed results with an "asymptotic" straight line of slope ½.

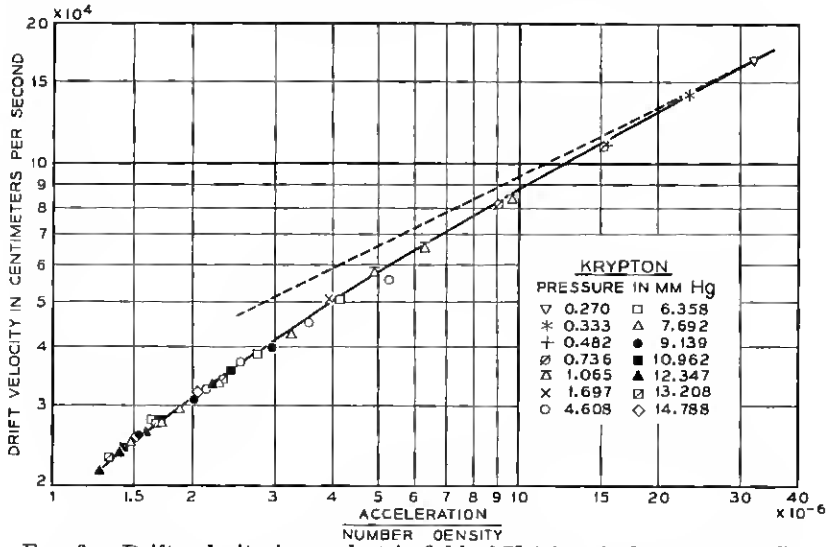

FIG. 6 — Drift velocity in an electric field of Kr^+ ions in krypton gas. Comparison of observed results with an "asymptotic" straight line of slope ½.

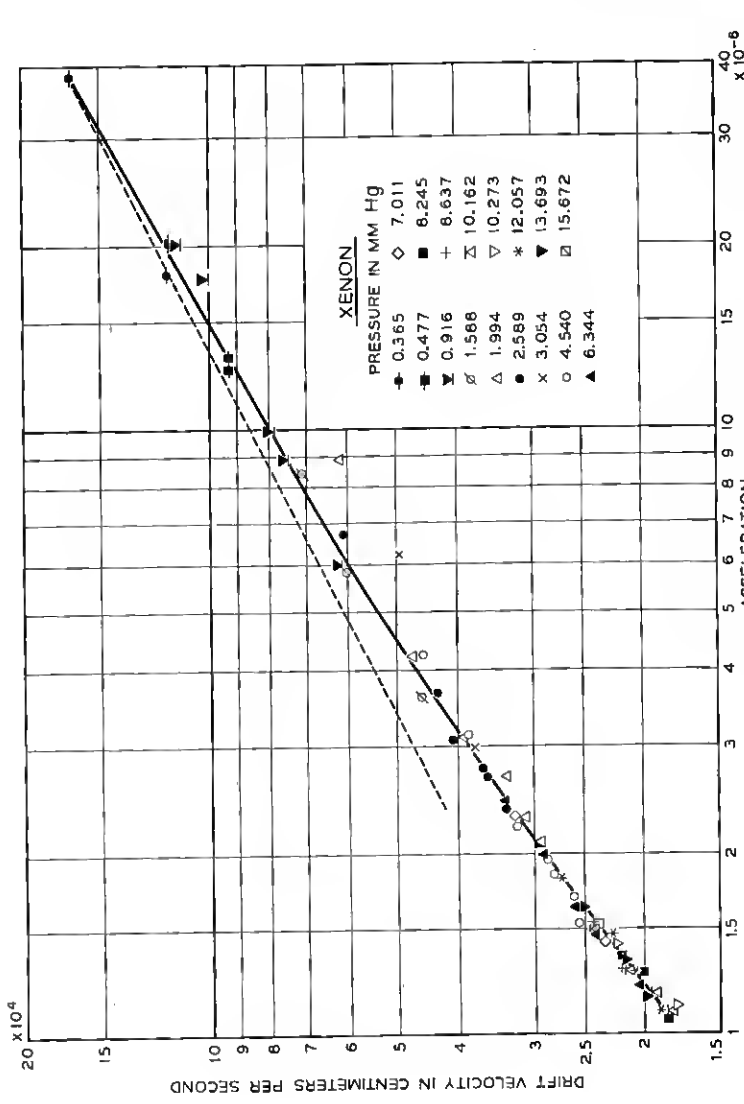

FIG. 7 — Drift velocity in an electric field of Xe^+ ions in xenon gas. Comparison of observed results with an "asymptotic" straight line of slope ½.

(26b) is required. The linear range of this plot is not as informative as the high field one. The slope unity is common to all formulas (27), and the temperature dependence of the mobility is needed to give the correct interpretation with the methods developed here. Tbere is a certain likelihood that the parameter α of equation (25) drifts from 0 to 1 as the speed of the ions is reduced; this was pointed out for the special case of He^+ in He in section IA. A qualitatively similar situation appears to prevail for the other noble gases.

Part II — The Motion of Uniform Ion Streams in the High Field Case

IIA. Formulations of the Boltzmann Equation

The dimensional analysis of the last section shows that there is an intrinsic simplicity to the high field case which is comparable to the low field case, while the intermediate case is more difficult. With one exception,[6] however, theoretical analysis has occupied itself with the low field case only. We shall try to remedy this in the following. To begin with, a tractable but accurate formulation of the problem has to be found. Such a formulation cannot treat the field term of equation (13) as a perturbation term, but must try instead to make use of the basically simple features of the problem, notably those exhibited by the dimensional analysis of Section ID.

The equation governing the high field properties of the ions is obtained simply by substituting δ-functions for the Maxwellian velocity distributions in equation (13). This gives

$$a\frac{\partial h(\mathbf{c})}{\partial c_z} + \frac{1}{\tau(c)}h(\mathbf{c}) = \frac{1}{4\pi}\iint \delta(\mathbf{C}')h(\mathbf{c}')\frac{1}{\tau(c')}\Pi(\chi)\,d\Omega_{\gamma'}\,d\mathbf{C} \qquad (31)$$

A reduction of the number of integrations from five to two must be possible in the integral term of (31), owing to the presence of the δ-function. To achieve this we must transform the variables of integration so as to make three of the differentials equal to $d\mathbf{C}'$. We do this in the following way. First observe that

$$\boldsymbol{\gamma} = \mathbf{c} - \mathbf{C}$$

and that $\mathbf{c}$ is a constant vector. Hence we may replace $d\mathbf{C}$ by $d\boldsymbol{\gamma}$. The five-fold integration reads then

$$d\Omega_{\gamma'}\,d\mathbf{C} = \gamma^2\,d\gamma\,d\Omega_{\gamma}\,d\Omega_{\gamma'} \qquad (32)$$

that is, it goes over the magnitude γ which the two vectors have in

common, and their orientations, for which they are independent. It is known that in integrating over the two angles defining an orientation the polar axis may be chosen freely. We shall, in the following, adopt $\mathbf{c}$ as our polar axis with ψ, κ being pole distances of γ and γ' to $\mathbf{c}$ and φ, ω the corresponding azimuths. In Fig. 8 these angles are exhibited on the unit sphere. All vectors are assumed to be plotted from the center of the sphere, and show up through their piercing points. The angles between the vectors then show up as sides and the azimuths as angles. The expression (32) becomes then

$$\gamma^2 \, d\gamma \sin \psi \, d\psi \, d\varphi \sin \kappa \, d\kappa \, d\omega$$

The main transformation consists now in introducing the three components of $\mathbf{C}'$ in the place κ, ψ and φ. The transformation formulas follow from the vector identity

$$\mathbf{C}' = \mathbf{c} - \frac{M}{M+m}\,\boldsymbol{\gamma} - \frac{m}{M+m}\,\boldsymbol{\gamma}' \tag{33}$$

and read in full

$$C_\xi' = -\frac{M\gamma}{M+m} \sin\psi \cos\varphi - \frac{m\gamma}{M+m} \sin\kappa \cos\omega$$

$$C_\eta' = -\frac{M\gamma}{M+m} \sin\psi \sin\varphi - \frac{m\gamma}{M+m} \sin\kappa \sin\omega$$

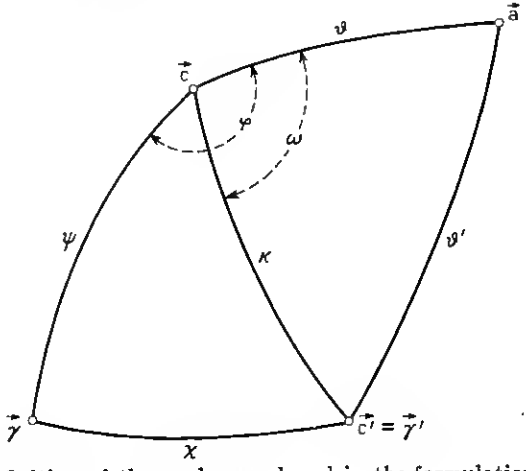

Fig. 8 — Definition of the angles employed in the formulations of the Boltzmann equation for the high field case.

$$C'_\zeta = -\frac{M\gamma}{M+m}\cos\psi - \frac{m\gamma}{M+m}\cos\kappa + c$$

From these equations the value of the Jacohian comes out to be

$$\frac{\partial(C'_\xi, C'_\eta, C'_\zeta)}{\partial(\kappa, \psi, \varphi)} = \frac{mM^2\gamma^3}{(M+m)^3}\sin\psi\,\{\cos\psi\sin\kappa - \sin\psi\cos\kappa\cos(\varphi-\omega)\}$$

We needs its value only at the position $C'_\xi = C'_\eta = C'_\zeta = 0$. If we take the above equations for C'_ξ, C'_η, C'_ζ and multiply them respectively by $\cos\kappa\cos\omega$, $\cos\kappa\sin\omega$, $-\sin\kappa$, add and set $\mathbf{C}' = 0$ we get the identity

$$\frac{M\gamma}{M+m}\{\cos\psi\sin\kappa - \sin\psi\cos\kappa\cos(\varphi-\omega)\} = c\sin\kappa$$

The curly hracket is exactly the one occurring in the Jacobian which therefore reduces to

$$\left[\frac{\partial(C'_\xi, C'_\eta, C'_\zeta)}{\partial(\kappa, \psi, \varphi)}\right]_{\mathbf{C}'=0} = \frac{Mm}{(M+m)^2}c'^2 c\sin\psi\sin\kappa$$

and hence

$$\gamma^2\,d\gamma\,d\Omega_\gamma\,d\Omega_{\gamma'} = \frac{(M+m)^2}{Mmc}\,d\mathbf{C}'\,dc'\,d\omega$$

Substituting finally this expression into (32) and (31) we get the Boltzmann equation in the form

$$a\frac{\partial h(\mathbf{c})}{\partial c_z} + \frac{1}{\tau(c)}h(\mathbf{c}) = \frac{(M+m)^2}{4\pi Mmc}\int_c^{\frac{M+m}{|M-m|}c}\frac{1}{\tau(c')}\,\Pi(\chi)\,dc'\int_0^{2\pi}h(\mathbf{c}')\,d\omega \tag{34}$$

The equation is in need of additional elucidation as regards the exact meaning of $\mathbf{c}'$ as a vector and as regards the auxiliary variable χ. As to the first point we may describe the integration as occurring over a surface in velocity space. This surface is obtained from the relation

$$\mathbf{C}' = 0 \qquad \mathbf{c}' = \boldsymbol{\gamma}' \tag{35}$$

which substituted into (33) becomes

$$(M+m)\mathbf{c} - m\boldsymbol{\gamma}' = M\boldsymbol{\gamma} \tag{36}$$

Squaring this and using (9) we get

$$(M - m)c'^2 + 2mc' \cdot \mathbf{c} - (M + m)c^2 = 0 \tag{37}$$

This is the equation of a sphere in velocity space which passes through the point $\mathbf{c}' = \mathbf{c}$. For all other points c' is bigger than c (collision with a stationary object always brings energy loss). The center of the sphere lies on the line joining $\mathbf{c}$ to the origin; it lies on the side of the origin from $\mathbf{c}$ when $m < M$, at infinity (making the sphere a plane) when $m = M$ and away from the origin when $m > M$. We make use of (37) to express the polar angle κ of $\mathbf{c}'$ with respect to $\mathbf{c}$ (which does not occur as an integration variable in (34)) in terms of c'. We get

$$\cos \kappa = \frac{(M + m)c^2 - (M - m)c'^2}{2mcc'} \tag{38}$$

The angle of scattering in the center of mass system also results from squaring of (36) if the term $m\gamma'$ is first taken to the right. We find

$$\cos \chi = \frac{(M + m)^2}{2Mm} \frac{c^2}{c'^2} - \frac{M^2 + m^2}{2Mm} \tag{39}$$

There is a more useful form of equation (34) which results if χ is taken as one of the integration variables rather than c'. Substitution is made from the equation (39) above; it yields

$$a \frac{\partial h(\mathbf{c})}{\partial c_z} + \frac{1}{\tau(c)} h(\mathbf{c}) = \frac{1}{4\pi} \int_0^\pi \sin \chi \, d\chi \frac{\Pi(\chi)}{\tau(c')} \left(\frac{c'}{c}\right)^3 \int_0^{2\pi} h(\mathbf{c}') \, d\omega \tag{40}$$

The magnitude of $\mathbf{c}'$ and its polar angle with respect to $\mathbf{c}$ are now auxiliary parameters; the first is obtained from (39)

$$c' = c \frac{M + m}{\sqrt{M^2 + m^2 + 2Mm \cos \chi}} \tag{41}$$

and the second from (38) and (41)

$$\cos \kappa = \frac{m + M \cos \chi}{\sqrt{M^2 + m^2 + 2Mm \cos \chi}} \tag{42}$$

As previously, the azimuth ω of $\mathbf{c}'$ about $\mathbf{c}$ is an independent variable.

The simplifications of the equation (31) exhibited in (34) and (40) still leave a double integral in the fundamental equation. The integration over $d\omega$ will now be eliminated by decomposition of $h(\mathbf{c})$ in spherical harmonics about the field direction. There is no loss of generality in this step.

$$h(\mathbf{c}) = \sum_{\nu=0}^{\infty} h_\nu(c) P_\nu (\cos \vartheta) \tag{43}$$

We have now to consider simultaneously the three vectors $\mathbf{c}$, $\mathbf{c}'$ and $\mathbf{a}$ as well as the angles between them. These angles are defined in Fig 8. We study equation (34) or (40) term by term in order to see what becomes of it upon substitution of (43). Starting with $h(\mathbf{c}')$ under the integral sign we get from Fig. 8 and the addition theorem for spherical harmonics

$$h(\mathbf{c}') = \sum_{\nu=0}^{\infty} h_\nu(c')[P_\nu(\cos\vartheta)P_\nu(\cos\kappa) + 2\sum_{\mu=1}^{\nu}\frac{(\nu-\mu)!}{(\nu+\mu)!}P_\nu^\mu(\cos\vartheta)P_\nu^\mu(\cos\kappa)\cos\mu\omega]$$

For this expression, the integration over ω is elementary and gives

$$\int_0^{2\pi} h(\mathbf{c}')\,d\omega = 2\pi\sum_{\nu=0}^{\infty} h_\nu(c')P_\nu(\cos\vartheta)P_\nu(\cos\kappa) \tag{44}$$

Further, we get for the derivative in (34) or (40)

$$\frac{\partial}{\partial c_x}\left(\sum_{\nu=0}^{\infty} h_\nu(c)P_\nu(\cos\vartheta)\right) = \sum_{\nu=0}^{\infty}\frac{dh_\nu(c)}{dc}\frac{1}{2\nu+1}\{(\nu+1)P_{\nu+1}(\cos\vartheta)+\nu P_{\nu-1}(\cos\vartheta)\} + \frac{1}{c}h_\nu(c)\frac{\nu(\nu+1)}{2\nu+1}\{P_{\nu-1}(\cos\vartheta)-P_{\nu+1}(\cos\vartheta)\} \tag{45}$$

Through the equations (43), (44) and (45), all terms in equation (34) or (40) are developed in spherical harmonics with respect to the angle ϑ between c and the field direction. We can therefore annul separately the coefficient of each Legendre polynomial in $\cos\vartheta$. This gives the following set of equations

$$\frac{(M+m)^2}{2Mmc}\int_c^{\frac{M+m}{|M-m|}c}\frac{h_\nu(c')}{\tau(c')}P_\nu(\cos\kappa)\,\Pi(\chi)\,dc' - \frac{h_\nu(c)}{\tau(c)} = \frac{\nu a}{2\nu-1}\left(\frac{dh_{\nu-1}(c)}{dc}-\frac{\nu-1}{c}h_{\nu-1}(c)\right) + \frac{(\nu+1)a}{2\nu+3}\left(\frac{dh_{\nu+1}(c)}{dc}+\frac{\nu+2}{c}h_{\nu+1}(c)\right) \tag{46}$$

or

$$\frac{1}{2}\int_0^\pi \frac{h_\nu(c')}{\tau(c')}\left(\frac{c'}{c}\right)^s P_\nu(\cos\kappa)\,\Pi(\chi)\sin\chi\,d\chi$$

$$-\frac{h_\nu(c)}{\tau(c)} = \frac{\nu a}{2\nu-1}\left\{\frac{dh_{\nu-1}(c)}{dc} - \frac{\nu-1}{c}h_{\nu-1}(c)\right\} \tag{47}$$

$$+\frac{(\nu+1)a}{2\nu+3}\left\{\frac{dh_{\nu+1}(c)}{dc} + \frac{\nu+2}{c}h_{\nu+1}(c)\right\}$$

where

$$\nu = 0, 1, 2, 3 \cdots .$$

The auxiliary parameters entering are given by (38) and (39) for equation (46), and (41) and (42) for equation (47).

The equations (46) or (47) obtained by Legendre decomposition still are, in general, mixed integral-differential equations in one independent variable. Further simplification is possible only in special cases some of which will be discussed later. An even more simple and tractable form of the Boltzmann equation can be achieved in general, however, if one gives up the idea of determining the velocity distribution function and concentrates instead on its moments. In other words, the Boltzmann equation can be looked upon as a system of relations between velocity averages, and as such it becomes a linear algebraic system.

To carry out this reduction we multiply equation (47) by c^{s+2} and integrate from 0 to ∞. The second term on the left is then a simple velocity average. The same is true on the right hand side if two integrations by part are permissible and leave no integrated out part. $s \geqq -1$ is probably adequate for this. The integral over the integral term at first looks as follows

$$\frac{1}{2}\int_0^\infty c^{s+2}\,dc\int_0^\pi \frac{h_\nu(c')}{\tau(c')}\left(\frac{c'}{c}\right)^s P_\nu(\cos\kappa)\,\Pi(\chi)\sin\chi\,d\chi$$

In this expression we pass from c to c' as the independent variable. From (41) we see that

$$\frac{dc}{c} = \frac{dc'}{c'}$$

Hence the expression becomes

$$\int_0^\infty c'^{s+2}\frac{h_\nu(c')}{\tau(c')}\,dc'\,\frac{1}{2}\int_0^\pi \left(\frac{c}{c'}\right)^s P_\nu(\cos\kappa)\,\Pi(\chi)\sin\chi\,d\chi$$

From (41) and (42) it is seen that this is actually the product of two independent integrals if the angular distribution $\Pi(\chi)$ is independent of the velocity of encounter c'. The first integral is then identical with the one arising from the second term in (47), and the second is a collision integral having no connection with the velocity distribution. Even if this is not the case, the second integral is still a dynamic average which can be evaluated as a function of c' previously to any knowledge of $h(c')$. We express this by introducing the abbreviation

$$I_{s,\nu} = \left(\frac{c}{c'}\right)^s P_\nu(\cos\kappa)$$

Using (41) and (42) we see that $I_{s,\nu}$ is the following function of χ

$$I_{s,\nu}(\chi) = \left(\frac{\sqrt{M^2 + m^2 + 2Mm\cos\chi}}{M+m}\right)^s \cdot P_\nu\left(\frac{m + M\cos\chi}{\sqrt{M^2 + m^2 + 2Mm\cos\chi}}\right) \tag{48a}$$

which, for the particular case of equal masses, takes the simple form

$$I_{s,\nu}(\chi) = \cos^s \tfrac{1}{2}\chi\, P_\nu(\cos\tfrac{1}{2}\chi) \tag{48b}$$

With this definition the integrated equation (47) reads

$$\int_0^\infty \left\langle \frac{1 - I_{s,\nu}(\chi)}{a\tau(c)} \right\rangle h_\nu(c) c^{s+2}\, dc = \frac{\nu(\nu+s+1)}{2\nu-1}\int_0^\infty h_{\nu-1}(c)c^{s+1}\, dc + \frac{(\nu+1)(s-\nu)}{2\nu+3}\int_0^\infty h_{\nu+1}(c)c^{s+1}\, dc$$

or in terms of averages

$$(2\nu+1)\left\langle \frac{1 - I_{s,\nu}(\chi)}{a\tau(c)} c^s P_\nu(\cos\vartheta)\right\rangle = \nu(\nu+s+1)\langle c^{s-1}P_{\nu-1}(\cos\vartheta)\rangle + (\nu+1)(s-\nu)\langle c^{s-1}P_{\nu-1}(\cos\vartheta)\rangle \tag{49}$$

I believe that equation (49) contains all possible derivable relations between averages as special cases. Some of the most notable ones are

listed below

$$s = 1, \qquad \nu = 1$$

$$\left\langle \frac{1 - \cos \chi}{a\tau(c)} c \cos \vartheta \right\rangle = \frac{M + m}{M} \tag{50a}$$

$$s = 2, \qquad \nu = 0$$

$$\left\langle \frac{1 - \cos \chi}{a\tau(c)} c^2 \right\rangle = \frac{(M + m)^2}{Mm} \langle c \cos \vartheta \rangle \tag{50b}$$

$$s = 2, \qquad \nu = 2$$

$$\left\langle \frac{3M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau(c)} c^2 P_2 (\cos \vartheta) \right\rangle = \frac{4(M + m)^2}{M} \langle c \cos \vartheta \rangle \tag{50c}$$

While the averages entering into (49) are not always the desired ones, it remains true nevertheless that all solution methods evolved in the following use this equation system as a starting point rather than other forms of the Boltzmann equation.

IIB. THE MEAN FREE TIME MODEL AT HIGH FIELD

If the angular distribution in the center of mass system is independent of speed and the collision cross section varies inversely as the speed then the developments of the previous section permit actually a solution of the Boltzmann equation. It is a solution in the sense that all significant velocity averages can be obtained directly without the knowledge of the velocity distribution function.

Before developing these facts from the equations of the last section, I should point out that the derivation to follow is in a sense artificial. It has been shown already by Maxwell[19] for related problems that if the mean free time between collisions is assumed constant specially simple techniques may be employed to get constants of experimental importance. These techniques can be employed here; they consist essentially in multiplying (13) by a suitable multiplier, followed by integration over c. However, if we were to follow this procedure we would have to duplicate for a special model in an unsystematic way the work done systematically for all laws of interactions in the preceding section. A further advantage of using systematic procedure is that we can see at a

[19] Maxwell, J. C., Collected Papers, Vol. II, p. 40.

glance what averages can or cannot be obtained, and what the relationship is between the high field and the general averages.

For this reason we limit ourselves at present to the high field averages obtainable from (49). For the special case under discussion this equation system takes the form

$$(2\nu+1)\left\langle\frac{1-I_{s,\nu}(\chi)}{a\tau}\right\rangle\langle c^s P_\nu(\cos\vartheta)\rangle = \nu(\nu+s+1)\langle c^{s-1}P_{\nu-1}(\cos\vartheta)\rangle + (\nu+1)(s-\nu)\langle c^{s-1}P_{\nu+1}(\cos\vartheta)\rangle \tag{51}$$

that is we have a system of linear relations connecting the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$. The connection between these averages is made apparent in Fig. 9. Each average $\langle c^s P_\nu(\cos\vartheta)\rangle$ is marked in this figure as a dot in an s-ν-plane if s is integer. The equations (51) connecting these averages are shown as lines with different equations leading to the same dot shown in different outline. These equations generally have the shape of a V;

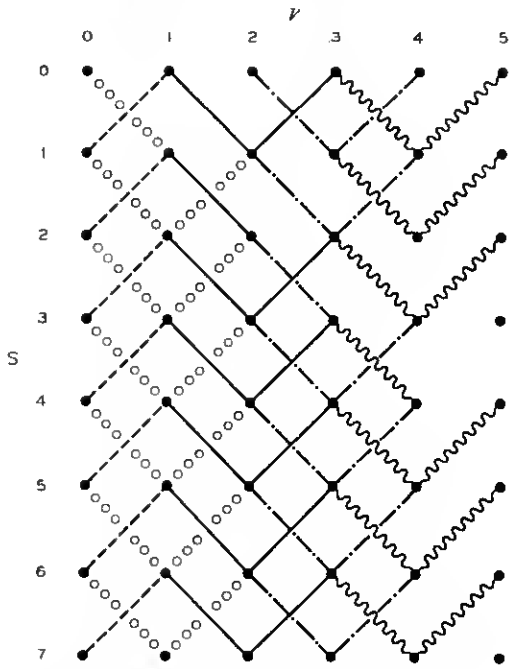

Fig. 9 — Interconnection established by the Boltzmann equation among the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$; case of constant mean free time.

there are two notable exceptions to this rule, however, which make the recurrence method possible, the equations $\nu = 0$ have no left leg and the equations $s = \nu$ have no right leg. Starting out with the average $s = 0$, $\nu = 0$, which equals unity by definition one can thus proceed systematically as shown in Fig. 10, to get other averages. The averages reached are the ones for which s and ν are non-negative integers of equal parity with the restriction $s \geqq \nu$. One verifies easily that this set is equivalent to the set of all products of integer powers of the velocity components.

The first three relations one uses in the path outlined in Fig. 10, are the simplified forms of the three equations (50). We find

$$\langle c_z \rangle = \frac{M + m}{M} \Big/ \left\langle \frac{1 - \cos \chi}{a\tau} \right\rangle \tag{52}$$

$$\langle c^2 \rangle = \frac{(M + m)^3}{M^2 m} \Big/ \left\langle \frac{1 - \cos \chi}{a\tau} \right\rangle^2 \tag{53}$$

$$\langle c^2 P_2 (\cos \vartheta) \rangle = \frac{4(M + m)^3}{M^2 \left\langle \dfrac{3M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle \left\langle \dfrac{1 - \cos \chi}{a\tau} \right\rangle}$$

or, more conveniently with the help of (53)

$$\langle c_z^2 \rangle = \frac{(M + m)^3 \left\langle \dfrac{M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle}{M^2 m \left\langle \dfrac{3M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle \left\langle \dfrac{1 - \cos \chi}{a\tau} \right\rangle^2} \tag{54}$$

The three equations (52), (53) and (54) give the drift velocity, the total energy, and the energy partition of the travelling ion. Equation (52) gives a constant mobility and can actually he derived from a low field theory. Formula (52) thus states that for problems involving a constant mean free time the high field and low field mobilities are numerically identical. One would suspect that the intermediate field value would have to fall in line too. This is indeed the case as will be shown in Section IIIA.

A convenient interpretation of (53) may be had by combining (52) and (53) in the following way

$$\langle mc^2 \rangle = m\langle c_z \rangle^2 + M\langle c_z \rangle^2 \tag{55}$$

The left side is essentially the total energy of the ion, the first term on the right is the energy visible in the drift motion; it follows therefore

that the second term is the "invisible" or random part of tbe mean energy. Formula (55) thus states that

$$\frac{\text{random energy}}{\text{visible energy}} = \frac{\text{molecular mass}}{\text{ion mass}} \tag{56}$$

that is, it exhibits in a quantitative way the capacity of storing energy in the form of random motion which light ions travelling in a heavy gas possess; for ions travelling in the parent gas the ordered and the random part of the energy are just equal; for heavy ions in a light gas the disordered fraction becomes negligible.

There are various ways of understanding the implications of equation (54). One way is to derive the mean energy in a direction at right angles to the field by the use of (53). We find

$$\langle c_x^2 \rangle = \frac{(M+m)^3 \left\langle \frac{\sin^2 \chi}{a\tau} \right\rangle}{Mm \left\langle \frac{3M \sin^2 \chi + 4m(1-\cos\chi)}{a\tau} \right\rangle \left\langle \frac{1-\cos\chi}{a\tau} \right\rangle^2} \tag{57}$$

Now from (54) and (57) the partition of the energy e may be obtained.

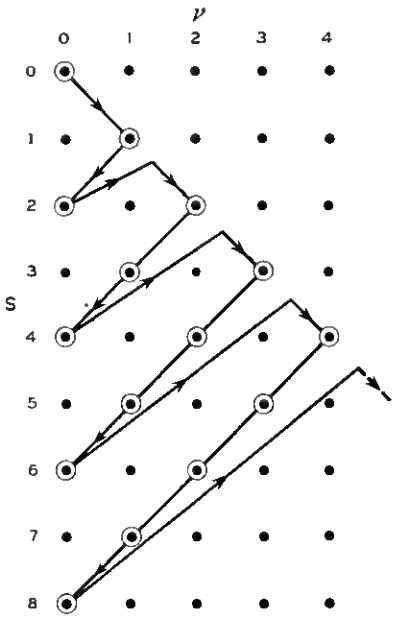

Fig. 10 — Order to be followed in computing by recursion the averages $\langle c^s P_\nu (\cos\vartheta) \rangle$; case of constant mean free time.

It comes out to be

$$e_x : e_y : e_z = \left\langle \frac{M \sin^2 \chi}{\tau} \right\rangle : \left\langle \frac{M \sin^2 \chi}{\tau} \right\rangle : \left\langle \frac{M \sin^2 \chi + 4m(1 - \cos \chi)}{\tau} \right\rangle \tag{58}$$

This shows up immediately the equipartition property for small m/M and the overwhelming preponderance of the motion in the field direction for large m/M. As an analysis of the random motion, however, equation (58) is deficient because the three directions become only comparable after the square of the drift velocity (52) is subtracted out of the z-component. We find

$$\langle c_z^2 \rangle - \langle c_z \rangle^2 = \frac{(M + m)^2 \left\langle \frac{M \sin^2 \chi + 2m(1 - \cos \chi)^2}{a\tau} \right\rangle}{Mm \left\langle \frac{3M \sin \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle \left\langle \frac{1 - \cos \chi}{a\tau} \right\rangle^2} \tag{59}$$

and from this a more refined partition formula which only counts random motion

$$e_x : e_y : e_z^* = \left\langle \frac{\sin^2 \chi}{\tau} \right\rangle : \left\langle \frac{\sin^2 \chi}{\tau} \right\rangle : \left\langle \frac{M \sin^2 \chi + 2m(1 - \cos \chi)^2}{(M + m)\tau} \right\rangle \tag{60}$$

For small m/M this result does not differ essentially from (58) but if m/M is large the z component of the random energy does not grow indefinitely the way the total energy does. Instead it stops at a value which is about four times one of the other two values.

A discussion of these expressions for special models will be delayed until the equations are extended to intermediate field conditions. This will be done in Part III.

IIC. THE CASE OF LARGE MASS RATIOS: ELECTRONS OR HEAVY IONS

The distribution of velocities for a small value of m/M is treated in the literature because it applies to electrons.[4,5] However, for the sake of completeness the derivation will be carried out here for the high field case. In this derivation all features of the law of scattering are left open, except that conservation of the kinetic energy is assumed.

The development in spherical harmonics carried out in Section IIA is the suitable starting point for small m/M, because, in this case, the distribution is almost spherically symmetrical and the expansion in spherical harmonics is also an expansion in powers of m/M. If we keep only $h_0(c)$ and $h_1(c)$ in the system (47) and treat m/M as small we get two equations, one for $\nu = 0$ and the one for $\nu = 1$. We may then use

(41) and (42) in the simplified form

$$\frac{c'}{c} \sim 1 + \frac{m}{M}(1 - \cos \chi) \tag{61}$$

$$\cos \kappa \sim \cos \chi + \frac{m}{M} \sin^2 \chi \tag{62}$$

and develop the equations in powers of m/M. Starting out with the simpler equation $\nu = 1$ we find

$$\left\langle \frac{1 - \cos \chi}{a\tau(c)} \right\rangle h_1(c) = -\frac{dh_0(c)}{dc} \tag{63}$$

This same procedure is not adequate for the equation $\nu = 0$ because the two left hand terms in (47) cancel in zero approximation. We must therefore develop the integral up to linear terms in m/M; this is a perfectly straightforward, though somewhat cumbersome, step. It leads to the following equation

$$\frac{m}{M}\left[c\frac{d}{dc}\left\{\left\langle \frac{1 - \cos \chi}{a\tau(c)} \right\rangle h_0(c)\right\} + 3\left\langle \frac{1 - \cos \chi}{a\tau(c)} \right\rangle h_0(c)\right] = \frac{1}{3}\left[\frac{dh_1(c)}{dc} + \frac{2}{c} h_1(c)\right]$$

The equation may be integrated by multiplication with c^2; this yields

$$h_1(c) = 3\frac{m}{M}\left\langle \frac{1 - \cos \chi}{a\tau(c)} \right\rangle c h_0(c) \tag{64}$$

Elimination of $h_1(c)$ from (63) and (64) gives a differential equation for $h_0(c)$ which is easily solved by quadrature; the result is

$$h_0(c) = \exp\left[-3\frac{m}{M}\int_0^c \left\langle \frac{1 - \cos \chi}{a\tau(c)} \right\rangle^2 c\, dc\right] \tag{65}$$

Except for the dependence on the angular law of scattering this formula may be found in the literature.[4] Its most important special cases are obtained for $\tau = \text{const}$ (Pseudo-Maxwellian distribution) and $\tau = \text{const}/c$ (Druyvesteyn distribution).

The derivation of (65) should be completed by a proof that indeed $h_2(c)$ is small compared to $h_1(c)$. This is not true for all values of c; on the contrary, the argument below shows that near the origin where $c \sim a\tau(c)$, $h_2(c)$ is actually comparable to $h_1(c)$. For our purposes, however, it is sufficient if it is true in the overwhelming majority of cases. As the proof applies equally to all h_ν's we will run it in this manner. Assuming

provisionally that

$$h_{\nu+1} \ll h_\nu \ll h_{\nu-1}$$

we see that we can drop the terms in $h_{\nu+1}$ in the system (47). The integral in (47) is evaluated in zero order with the help of (61) and (62); it becomes then

$$\frac{h_\nu(c)}{\tau(c)} \cdot \frac{1}{2} \int_0^\pi P_\nu(\cos\chi)\Pi(\chi) \sin\chi \, d\chi$$

This means that we may solve explicitly for $h_\nu(c)$ in terms of $h_{\nu-1}(c)$. The formula is

$$h_\nu(c) \approx \frac{\nu}{2\nu - 1} \frac{-\frac{dh_{\nu-1}(c)}{dc} + \frac{\nu - 1}{c} h_{\nu-1}(c)}{\left\langle \frac{1 - P_\nu(\cos\chi)}{a\tau(c)} \right\rangle} \tag{66}$$

To estimate the order of magnitude of this we may neglect $P_\nu(\cos\chi)$ as compared to 1 and assume ν large. The operation in the numerator will lead to two kinds of terms: some of the form

$$\frac{1}{c} h_{\nu-1}(c)$$

and others of the type

$$\frac{m}{M} \frac{c}{\{(a\tau(c)\}^2} h_{\nu-1}(c)$$

coming from differentiation of an exponent of the type (65). Now we find from (65) that the overwhelming majority of particles have speeds c which in order of magnitude satisfy

$$c \sim (M/m)^{1/2} a\tau(c) \tag{67}$$

because this is the range within which the exponent remains comparable to 1. Applying this to the two types of terms arising from (66) we find for them in order of magnitude

$$\nu a\tau(c) \frac{1}{c} h_{\nu-1}(c) \sim \nu \left(\frac{m}{M}\right)^{1/2} h_{\nu-1}(c)$$

and

$$a\tau(c) \frac{m}{M} \frac{c}{\{(a\tau(c)\}^2} h_{\nu-1}(c) \sim \left(\frac{m}{M}\right)^{1/2} h_{\nu-1}(c)$$

If we substitute this into (66) we see that the h_ν's decrease as $(m/M)^{\frac{1}{2}\nu}$, with a possible $\nu!$ slowing up the final convergence. In any case $h_2(c)$ comes out small compared to $h_1(c)$ which is all that is needed to make equation (65) approximately correct.

While the case of small m/M is generally known it appears to be otberwise for large m/M. The intuitive basis for the solution of this case is the fact observable from (52), (57) and (59) that $\langle \mathbf{c} \rangle$ increases indefinitely with m/M, hut that the relative deviation from the mean decreases so that the distribution function approaches a δ-function. The structure of this limiting function may be explored, starting directly from (40), hecause in the limit of large m/M the sphere of integration shrinks as may be verified from (37). This makes it possihle to replace the integral in (40) hy differential terms. This becomes clearer if (40) is written in the form

$$a \frac{\partial h(\mathbf{c})}{\partial c_z} = \frac{1}{2} \int_0^\pi \Pi(\chi) \sin \chi \, d\chi \frac{1}{2\pi} \int_0^{2\pi} d\omega \left\{ \left(\frac{c'}{c}\right)^3 \frac{h(\mathbf{c}')}{\tau(c')} - \frac{h(c)}{\tau(c)} \right\} \tag{68}$$

Let us call the inner average $\mathcal{J}$. It exhibits the differential properties discussed earlier: the curly hracket is the difference of two terms which are almost identical. Hence we approximate the value of $\mathcal{J}$ by expanding the slowly varying terms to first order in $\mathbf{c}' - \mathbf{c}$, while the fast varying $h(\mathbf{c}')$ will be expanded to square terms. This expansion is obviously permissible for everything except the rapidly varying function $h(\mathbf{c}')$. For $h(\mathbf{c}')$ itself no justification can be offered except success. By proceeding to square terms in this expansion we mitigate any possible error committed, hut it is quite possible that structural details are lost in the procedure.

The development of $\mathcal{J}$ is straightforward. We proceed as follows

$$\begin{aligned} \mathcal{J} &= \frac{1}{2\pi} \int_0^{2\pi} d\omega \left\{ h(\mathbf{c}) \left(\left(\frac{c'}{c}\right)^3 \frac{1}{\tau(c')} - \frac{1}{\tau(c)} \right) + \left(\frac{c'}{c}\right)^3 \frac{1}{\tau(c')} \left(h(\mathbf{c}') - h(\mathbf{c})\right) \right\} \\ &\approx h(\mathbf{c}) \left\{ \left(\frac{c'}{c}\right)^3 \frac{1}{\tau(c')} - \frac{1}{\tau(c)} \right\} + \frac{1}{\tau(c)} \cdot \frac{1}{2\pi} \int_0^{2\pi} d\omega \, \{h(\mathbf{c}') - h(\mathbf{c})\} \end{aligned}$$

The expansion of the first term involves only (41) which to this order reads

$$c' - c \approx c \frac{M}{m} (1 - \cos \chi)$$

This formula does not contain the azimuth ω which therefore disappears trivially. In the second term on the contrary we are dealing with a vectorial difference involving all three polar coordinates c', κ, ω of $\mathbf{c}'$.

If we set

$$c_\xi' = \mathbf{c}' \sin \kappa \cos \omega$$

$$c_\eta' = c' \sin \kappa \sin \omega$$

$$c_\zeta' = c' \cos \kappa$$

we find

$$h(\mathbf{c}') - h(\mathbf{c}) = \frac{\partial h(\mathbf{c})}{\partial c_\xi} c_\xi' + \frac{\partial h(\mathbf{c})}{\partial c_\eta} c_\eta' + \frac{\partial h(\mathbf{c})}{\partial c_\zeta} (c_\zeta' - c) + \frac{1}{2} \frac{\partial^2 h(\mathbf{c})}{\partial c_\xi^2} c_\xi'^2$$
$$+ \frac{1}{2} \frac{\partial^2 h(\mathbf{c})}{\partial c_\eta^2} c_\eta'^2 + \frac{1}{2} \frac{\partial^2 h(\mathbf{c})}{\partial c_\zeta^2} (c_\zeta' - c)^2 + \frac{\partial^2 h(\mathbf{c})}{\partial c_\xi \partial c_\eta} c_\xi' c_\eta'$$
$$+ \frac{\partial^2 h(\mathbf{c})}{\partial c_\xi \partial c_\zeta} c_\xi'(c_\zeta' - c) + \frac{\partial^2 h(\mathbf{c})}{\partial c_\eta \partial c_\zeta} c_\eta'(c_\zeta' - \mathbf{c}) + \cdots$$

With the formulas given, integration over ω is elementary. We find

$$\mathcal{J} \approx h(\mathbf{c}) \left\{ \left(\frac{c'}{c} \right)^3 \frac{1}{\tau(c')} - \frac{1}{\tau(c)} \right\} + \frac{1}{\tau(c)} \left\{ \frac{\partial h(\mathbf{c})}{\partial c_\zeta} (c' \cos \kappa - c) \right.$$
$$\left. + \frac{1}{4\tau(c)} \left(\frac{\partial^2 h(\mathbf{c})}{\partial c_\xi^2} + \frac{\partial^2 h(\mathbf{c})}{\partial c_\eta^2} \right) c'^2 \sin^2 \kappa + \frac{1}{2\tau(c)} \frac{\partial^2 h(\mathbf{c})}{\partial c_\zeta^2} (c' \cos \kappa - c)^2 \right\}$$

All coefficients are to be evaluated only to the lowest non-vanishing order in M/m. From the equations (41) and (42) we get

$$c' \cos \kappa - c \approx (M/m)\, c(1 - \cos \chi)$$

$$c'^2 \sin^2 \kappa \approx (M/m)^2 c^2 \sin^2 \chi$$

The first term in $\mathcal{J}$ is simplified further by introduction of the parameter α used in the dimensional analysis of Section ID. According to that section we have that

$$\frac{d \ell n \tau(c)}{d \ell n c} = -1 + \alpha \tag{69}$$

We can generalize the original definition for any $\tau(c)$ by the above equation, where α is now a function of c. Eliminating also the tempo-

rary device of a ξ, η, ζ coordinate system we find for $\mathcal{J}$:

$$\mathcal{J} = \frac{M}{m}(4 - \alpha(c))(1 - \cos\chi)\frac{h(\mathbf{c})}{\tau(c)} + \frac{M}{m}\frac{(1 - \cos\chi)}{\tau(c)}\left\{c_x\frac{\partial h}{\partial c_x} + c_y\frac{\partial h}{\partial c_y} + c_z\frac{\partial h}{\partial c_z}\right\} + \left(\frac{M}{m}\right)^2\frac{\sin^2\chi}{4\tau(c)}\left\{\frac{\partial^2 h}{\partial c_x^2} + \frac{\partial^2 h}{\partial c_y^2} + \frac{\partial^2 h}{\partial c_z^2}\right\} + \left(\frac{M}{m}\right)^2\frac{2(1 - \cos\chi)^2 - \sin^2\chi}{4\tau(c)}\, c\left\{c_x\frac{\partial}{\partial c_x} + c_y\frac{\partial}{\partial c_y} + c_z\frac{\partial}{\partial c_z}\right\} \cdot \left\{\frac{c_x}{c}\frac{\partial h}{\partial c_x} + \frac{c_y}{c}\frac{\partial h}{\partial c_y} + \frac{c_z}{c}\frac{\partial h}{\partial c_z}\right\}$$

If the last term is evaluated exactly terms of the order $(M/m)^2$ are added to the first derivative terms in $h(\mathbf{c})$. They are obviously negligible. Finally integration over χ yields the following form for equation (68)

$$a\frac{\partial h(\mathbf{c})}{\partial c_z} = \langle\mathcal{J}\rangle = \frac{M}{m}\left\langle\frac{1 - \cos\chi}{\tau(c)}\right\rangle\{4 - \alpha(c)\}h(\mathbf{c}) + \frac{M}{m}\left\langle\frac{1 - \cos\chi}{\tau(c)}\right\rangle\sum_{i=1}^{3} c_i\frac{\partial h}{\partial c_i} + \frac{1}{4}\left(\frac{M}{m}\right)^2\left\langle\frac{\sin^2\chi}{\tau(c)}\right\rangle c^2\sum_{i=1}^{3}\frac{\partial^2 h}{\partial c_i^2} + \frac{1}{4}\left(\frac{M}{m}\right)\left\langle\frac{(1 - \cos\chi)(1 - 3\cos\chi)}{\tau(c)}\right\rangle\sum_{i,k=1}^{3} c_i c_k\frac{\partial^2 h}{\partial c_i \partial c_k} \tag{70}$$

When equation (70) is considered up to linear terms in M/m it yields a δ-function about the drift velocity $\langle c_z\rangle$ wbicb results from the implicit equation

$$\langle c_z\rangle = \frac{m}{M}\, a \Big/ \left\langle\frac{1 - \cos\chi}{\tau(c)}\right\rangle_{c=\langle c_z\rangle} \tag{71}$$

The δ-function takes here the aspect of a non integrable function which in a special case can be seen to equal

$$h \approx \{c_x^2 + c_y^2 + (c_z - \langle c_z\rangle)^2\}^{-3/2}$$

When normalization is imposed on such a function it is made to vanisb everywhere except at the point corresponding to the drift velocity.

The square terms in M/m are necessary to gain information about the functional form of $h(c)$. Since the region in velocity space in which h is appreciable is still small we may take α as constant in that region. A further simplication results from order of magnitude considerations on $\mathbf{c}$:

$$c^2 \sim c_z^2 \sim \langle c_z\rangle^2 \gg c_x^2 \sim c_y^2 \sim (c_z - \langle c_z\rangle)^2$$

In working out the details we see that division by

$$\frac{M}{m}\left\langle\frac{1-\cos\chi}{\tau(c)}\right\rangle$$

puts the first two terms on the right hand side of (70) in a simple form. The coefficient of the field term becomes then

$$\frac{am}{M\left\langle\frac{1-\cos\chi}{\tau(c)}\right\rangle}=\frac{am}{M\left\langle\frac{1-\cos\chi}{\tau(c)}\right\rangle_{c=\langle c_z\rangle}}\cdot\left(\frac{\langle c_z\rangle}{c}\right)^{1-\alpha}$$

The first factor is just $\langle c_z\rangle$ by the identity (71). For the second factor we have up to linear small terms

$$c=\sqrt{c_x^2+c_y^2+c_z^2}=\sqrt{c_x^2+c_y^2+(\langle c_z\rangle+c_z-\langle c_z\rangle)^2}$$

$$\approx\langle c_z\rangle\left\{1+\frac{c_z-\langle c_z\rangle}{\langle c_z\rangle}\right\}$$

and hence for the coefficient of the field term

$$\langle c_z\rangle\left(\frac{\langle c_z\rangle}{c}\right)^{1-\alpha}\approx\langle c_z\rangle-(1-\alpha)(c_z-\langle c_z\rangle)$$

After division by

$$\frac{M}{m}\left\langle\frac{1-\cos\chi}{\tau(c)}\right\rangle,$$

the square terms still contain another small factor M/m; it appears sufficient, therefore, to keep only the leading terms which are the ones containing $\langle c_z\rangle^2$ as factor. All these terms are multiplied with the ratio of two angular averages over $d\chi$; these may be taken as independent of c to a good approximation. Equation (70) thus takes the form

$$(4-\alpha)h(\mathbf{c})+c_x\frac{\partial h(\mathbf{c})}{\partial c_x}+c_y\frac{\partial h(\mathbf{c})}{\partial c_y}+(2-\alpha)(c_z-\langle c_z\rangle)\frac{\partial h(\mathbf{c})}{\partial c_z}$$

$$+\frac{1}{4}\frac{M}{m}\frac{\left\langle\frac{\sin^2\chi}{\tau}\right\rangle}{\left\langle\frac{1-\cos\chi}{\tau}\right\rangle}\langle c_z\rangle^2\left\{\frac{\partial^2 h(\mathbf{c})}{\partial c_x^2}+\frac{\partial^2 h(\mathbf{c})}{\partial c_y^2}\right\}\tag{72}$$

$$+\frac{1}{2}\frac{M}{m}\frac{\left\langle\frac{(1-\cos\chi)^2}{\tau}\right\rangle}{\left\langle\frac{(1-\cos\chi)}{\tau}\right\rangle}\langle c_z\rangle^2\frac{\partial^2 h(\mathbf{c})}{\partial c_z^2}=0$$

The equation can be solved explicitly in Cartesian coordinates by the method of separation of variables. The result is

$$h(\mathbf{c}) = \exp\left[-2\frac{m}{M}\frac{\left\langle\frac{1-\cos\chi}{\tau}\right\rangle}{\left\langle\frac{\sin^2\chi}{\tau}\right\rangle}\frac{c_x^2+c_y^2}{\langle c_z\rangle^2} - (2-\alpha)\frac{m}{M}\frac{\left\langle\frac{1-\cos\chi}{\tau}\right\rangle}{\left\langle\frac{(1-\cos\chi)^2}{\tau}\right\rangle}\frac{(c_z-\langle c_z\rangle)^2}{\langle c_z\rangle^2}\right] \tag{73}$$

This is a Maxwellian distribution with elliptic distortion and shifted origin, that is, the type shown in Fig. 1 (b).

The result (73) indicates the main features of the solution for heavy ions. Because of the neglect of derivatives higher than the second in $h(\mathbf{c}')$ it is not certain that (73) is correct in all details, even in the limit of very large m/M.

IID. THE CASE OF EQUAL MASSES; IONS TRAVELLING IN THE PARENT GAS

The developments of the previous section show that if the ion mass is either large or small in comparison to the molecular mass, analytical methods can be applied successfully to determine the velocity distribution of the ions. No such possibility was found for the mass ratio unity, which one would judge to be of particular interest because it applies to ions travelling in the parent gas. There exist isolated fragments of such an analytical theory; for instance, if we assume isotropic scattering in (46), that is $\Pi(\chi) = 1$, then the zeroth equation (46) becomes explicitly integrable and yields

$$h_0(c) = -\frac{1}{3}a\tau(c)\frac{dh_1(c)}{dc} \tag{74}$$

This is a curious reversal of the differential relationship (63) derived for electrons and implies a rather strong condition on the structure of $h_1(c)$. However, I have not been able to consolidate these fragments into something which can be used successfully in computation. The high field distribution function for mass ratio unity appears, however, sufficiently interesting to warrant the use of other methods.

A numerical determination of the velocity distribution function was undertaken in cooperation with R. W. Hamming by the so-called Monte Carlo method. The Monte Carlo method is a way of gaining

statistical information about a system hy following an individual member through a large number of random processes. The result of such a procedure is knowledge about one member of the assembly for a long period of time. Time averages of various kinds can be ohtained from such data; tbese time averages are then set equal to instantaneous averages over the assemhly, in accordance with ergodic theory. In our case, an ion was followed through 10,000 collisions. On an average, the collisions were isotropic in the center of mass system ($\Pi(\chi) = 1$) and obeyed a mean free time condition $\tau = \text{const}$. Actually, both the free time and the scattering angles varied from collision to collision; the angles varied in a random fashion over a unit sphere and τ was random within an exponential distribution.

A Monte Carlo calculation of tbis type consists of three parts. In the first part the random numbers having the required distributions are obtained and recorded. In the present problem there were three such random numbers required for each collision, namely a time and two angles. These numbers were placed on 10,000 IBM cards, along with suitable identification. In the second part a calculating machine simulates the successive collisions and keeps a record of the initial and final velocities for each one. The third part consists in analyzing statistically the numerical material accumulated in the second. For the first part of the calculation particular values must be chosen for the acceleration a and the mean free time τ. These values were

$$a = 1$$

$$\tau = \log_{10} e = 0.43429$$

However, the dimensional analysis of Section ID shows us at this point that these two constants enter into the problem only through their product $a\tau$ which scales all velocities. It is therefore convenient at the statistical stage to remove these factors and to analyze the results in terms of a dimensionless variahle which by (26c) we take in the form

$$\mathrm{w} = \frac{\mathrm{c}}{a\tau} \tag{75}$$

In view of the a priori information for mean free time problems which is gathered in Section IIB we can use the statistical data from the Monte Carlo calculation in two ways. We may (a) check the numerical computation itself or (b) gain new information not available otherwise.

(a) Tbe check of the numerical calculation hy statistical analysis proceeds as follows. From deductive reasoning we have obtained the

averages (52), (54) and (57) for c_z, c_x^2 and c_z^2. These formulas ought to be verified in the Monte Carlo calculation. This is indeed approximately true. A sampling covering 9492 out of the 10,000 collisions gives

	by Monte Carlo	by deduction
$\langle w_z \rangle$	1.912	2
$\langle w_x^2 \rangle$	0.801	$\frac{8}{9} = 0.889$
$\langle w_z^2 \rangle$	5.165	$\frac{56}{9} = 6.222$

The agreement is essentially there but deviations are noticeable. In judging these we have to realize that fluctuations are quite large in this problem. For instance if the calculation is broken down into ten runs of approximately 1,000 events each one finds the following time averages for the partial runs:

	$\langle w_z \rangle$	$\langle w_x^2 \rangle$	$\langle w_z^2 \rangle$
	1.821	0.837	4.453
	1.975	0.748	5.531
	1.915	0.785	5.132
	1.954	0.829	5.441
	1.868	0.731	4.794
	2.003	0.807	5.581
	1.766	0.793	4.811
	1.962	0.827	5.360
	2.003	0.901	5.471
	1.914	0.727	5.200
predicted	2.000	0.889	6.222

Among these runs there are some having averages higher than the predicted values, but the data clearly show that the Monte Carlo averages are generally lower. In the search for reasons it was first felt that perhaps the desired mean value for τ is not actually reached, perhaps through systematic errors introduced by the operator when rejecting certain runs. This seems indeed to be the case. The mean free time obtained from the 9492 runs mentioned above is

$$\tau = 0.4269$$

which is slightly low. Indeed it is observed that the runs with high τ were particularly troublesome in the calculation and were preferably rejected by the operator. It seems doubtful however that this error

could account for the entire discrepancy, particularly in the mean squares, although it must be emphasized that the runs with high τ make a more than proportional contribution to the total average. The angles of scattering have not been subjected to a similar analysis so that we cannot make a statement whether the aimed at isotropy in the law of scattering was realized or not. We conclude therefore by saying that while the Monte Carlo calculation gives results in general agreement with the deductive theory there are small but noticeable systematic errors in it whose origin is only partly explained. Similar errors must exist in the new results which cannot be compared with theoretical predictions.

(b) In this part we will discuss the velocity distribution function which may be constructed from the Monte Carlo results. In constructing such a function we make use of the fact that, between collisions, the velocity is accelerated at a uniform rate. Thus, in each period between two collisions, the velocity vector traces out a straight line parallel to the w_z axis covering equal distances in equal times. The Monte Carlo calculation furnishes us with a number of such straight lines as shown in Fig. 11. The density of these straight line tracks in velocity space is the velocity distribution function. The actual procedure used to obtain it was to lay a grid with a mesh of 0.23 in a half-plane with coordinates w_z and $w_\rho = \sqrt{w_x^2 + w_y^2}$ and to count the number of lines crossing each horizontal square edge. When the resultant count is converted to density

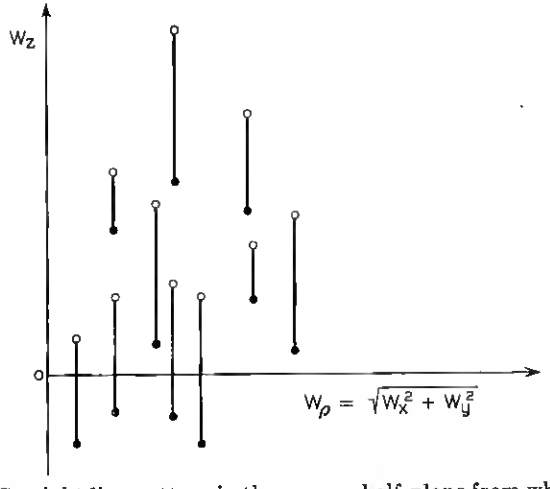

Fig. 11 — Straight line pattern in the $w_z - w_\rho$ half plane from which the velocity distribution is constructed; the Monte Carlo calculation furnishes the initial and final velocities (dots and rings).

and normalized to 1 we get a distribution in the $w_z - w_\rho$ half plane which is shown in Fig. 12. Division by $2\pi w_z$ will transform it into a conventional distribution function in velocity space; a plot of this function is shown in Fig. 13. What distinguishes this distribution function from functions previously proposed is the elongated probability contours. This feature is not unexpected in view of the unequal energy partition apparent in the equations (58) and (60).

The probability contours shown in Figs. 12 and 13 give a reliable general picture but we must not expect from them fine detail. Indeed we will now prove that the distribution function is infinite along the entire positive c_z-axis, a feature which is not obvious from inspection of Fig. 13.

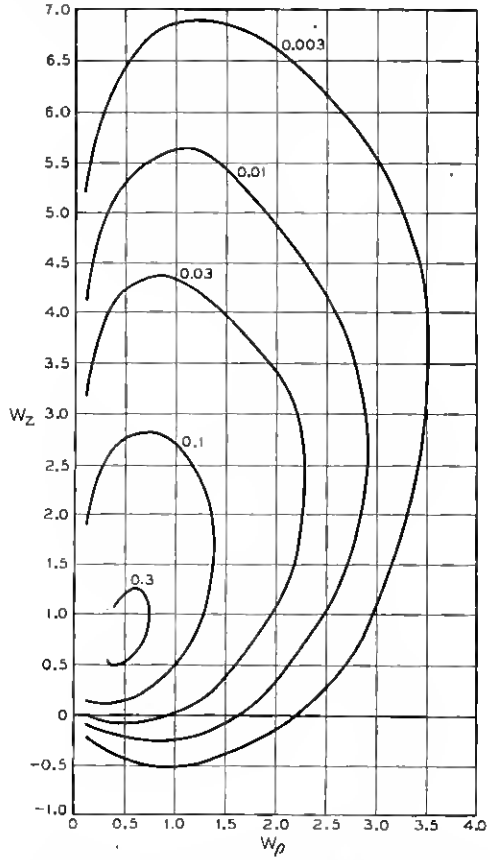

Fig. 12 — Motion of ions through the parent gas in a high field; distribution of velocities in the $w_z - w_\rho$ half plane resulting from the Monte Carlo calculation.

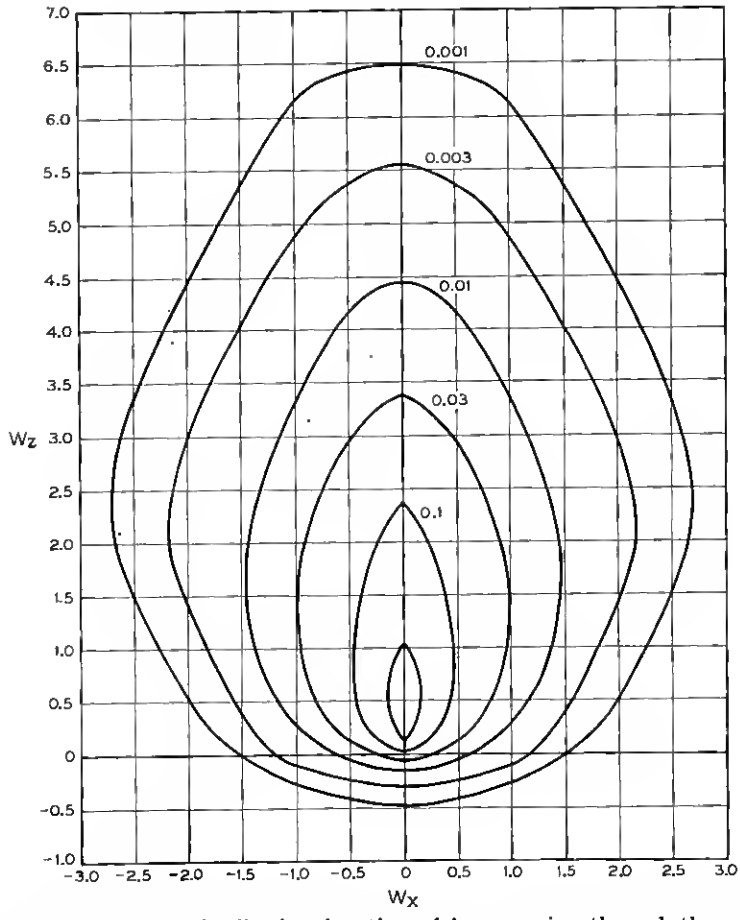

Fig. 13 — Velocity distribution function of ions moving through the parent gas in a high field; contours constructed from the Monte Carlo results of Fig. 12.

A simple physical proof of this statement goes as follows. Suppose an ion and a molecule make a collision which is almost central, but has a small impact parameter b. The collision will bring the ion almost to rest because the atom was originally at rest by hypothesis. Because the collision was not quite central, however, the ion will have a small residual velocity $\mathbf{c}_f$ at right angles to its original velocity $\mathbf{c}_i$. For any reasonable law of scattering this quantity c_f will be proportional to c_i and to b.

$$c_f \propto c_i \cdot b$$

The probability for a value of b between b and $b + db$ is proportional

to $b\ db$. Thus even if all c_i's were equally probahle the probability for c_f would vary as $c_f\,dc_f$. Actually very small c_i's may be specially probable as the theorem states and this fact may or may not increase the probahility for small c_f. This means that $P(c_f)dc_f$ probably varies as $c_f dc_f$, and may perhaps even contain a smaller power of c_f. When such a probability function is plotted in velocity space it will vary as $1/c_f$. Thus we know that the distribution function $\varphi(\mathbf{c})$ for ions immediately following a collision has a singularity at the origin at least as $1/c_f$. The actual distribution function $h(\mathbf{c})$ is derived from this one by spreading each point out in the forward direction as shown in Fig. 11. For the mean free time case we can write this out explicitly in the form

$$h(\mathbf{c}) = \frac{1}{\tau}\int_0^\infty \varphi(\mathbf{c} - \mathbf{a}t)\, e^{-\frac{t}{\tau}}\, dt \qquad (76)$$

For the case of a mean free path or other laws the formula is more awkward but they all differ from the above only in replacing $e^{-\frac{t}{\tau}}$ by a more complicated weight function. The singularity of h arises out of the singularity of φ which contains at least a factor $1/\sqrt{c_x^2 + c_y^2 + (c_z - at)^2}$. Along the c_z-axis, this become a factor $1/(c_z - at)$; this factor makes the integral diverge for all positive c_z; as we approach the origin from negative c_z's the distribution function will become infinite at least as $\ell n\ 1/c_z$.

The reasoning given is intrinsicly classical because of the use of "infinitely small" impact parameters. We should not hasten to conclude, however, that the quantization of the angular momentum will necessarily remove the singularity. Indeed we know that the only mechanical information which has to be put into the Boltzmann equation (31) is the differential cross-section for scattering. If this quantity does not differ essentially in the 180° direction from a classical cross section then it will not modify the conclusion we have reached.

Conclusions which are more informative, but less "anschaulich" may he obtained from a study of Boltzmann's equation either in its closed form (34) or (40) or its "Legendre" form (46) or (47). In view of the proof given we will give only an outline of the reasoning. First we can remove the second term in (40) by the substitution

$$h(\mathbf{c}) = \exp\left[-\int_0^{c_z} \frac{dc_z}{a\tau(c)}\right] h^*(\mathbf{c})$$

The exponential is easily seen to be always positive and finite for finite c. The Boltzmann equation then takes the form

$$\exp\left[-\int_0^{c_z} \frac{dc_z}{a\tau(c)}\right] a\,\frac{\partial h^*}{\partial \mathbf{c}_z} = \frac{1}{\mathbf{c}}\cdot(\text{an integral})$$

For equal masses the integral on the right runs over a plane in velocity space. Its integrand is always positive; hence the integral can never vanish and is always positive; it is conceivable that it could be infinite for a special position provided the infinity is integrable. Such an infinity would only make matters worse. At any rate the equation shows that $h^*(c)$ increases monotonely with increasing c_z. When we approach the origin from negative c_z we get a logarithmic divergence (or worse). As the function $h^*(c)$ can nowhere decrease with increasing c_z the infinity along the positive c_z axis is confirmed and its logarithmic nature is made very likely.

Information obtainable from equation (46) confirms this conclusion. Lowest powers in the entire recursion system can be made to cancel by assuming that for small c

$$h_0 \sim -A \ell n w$$

$$h_i \sim B_i \qquad i > 0$$

with suitable relationships existing between these quantities.

A defect of all three approaches is that they give no information concerning the nature of the infinity for $c_z > 0$. One is tempted to conclude from Fig. 13 that it cannot be very strong. Something like a singularity is discernible at the origin, particularly if the contour 0.1 is drawn back to cut the w_z-axis at a negative value; this is perfectly compatible with the available information. For large positive w_z, on the other hand, the picture almost contradicts the theorem just proved. One concludes from this that the singularity, for large c_z, becomes a weak and narrow ridge rising more or less abruptly in an otherwise well behaved function.

IIE. THE CASE OF EQUAL MASSES; A NEW COMPUTATIONAL PROCEDURE

The foregoing sections have accumulated substantial evidence that there are many analytical details involved when one discusses the structure of a velocity distribution function. These details are of little interest to the experimenter who may want nothing but a formula for the drift velocity or the average energy. In view of this situation it appears very desirable to find a method whereby such quantities can be derived directly and accurately from the Boltzmann equation without a full knowledge of the entire distribution.

Maxwell's original work shows us how to achieve this for molecules obeying the mean free time condition of Section IIB. In the following, a general method is described which will permit determination of such

averages for au arbitrary law of force between the ions and the gas molecules, and an arbitrary mass ratio. The application will be limited to the case of tbe mass ratio 1 whose study was begun in tbe preceding section.

The basis of the metbod is an observation on the equation system (46) or (47), which is the form taken by the Boltzmann equation after inserting the Legendre decomposition (43). It would appear at first sight that these recursion relations are of such a structure that an arbitrary function $h_0(c)$ could be substituted into the "zeroth" equation and that the relations would then successively determine h_1, h_2, $h_3 \cdots$. Upon closer inpsection this is found not to be the case. Suppose we have obtained somehow functions h_0, h_1, $h_2 \cdots h_n$ and we are trying to use the nth equation to determine h_{n+1}. This equation is of the form

$$\frac{dh_{n+1}}{dc} + \frac{n+2}{c} h_{n+1} = \text{known material} \tag{77}$$

We solve for h_{n+1} by multiplying with c^{n+2} and integrating. This gives

$$c^{n+2} h_{n+1}(c) = \int^c (\text{known material})\, dc$$

The left-hand side is of such a structure that it must vanish both for $c = 0$ and $c = \infty$. It follows that tbe right-hand integral when taken between the limits 0 and ∞ must equal zero. This condition is indeed obeyed for any $h_0(c)$ when $n = 0$. The integral condition reads in this case

$$\frac{1}{2} \int_0^\infty c^2\, dc \int_0^\pi \Pi(\chi) \sin \chi\, d\chi \frac{h_0(c')}{\tau(c')} \left(\frac{c'}{c}\right)^3 - \int_0^\infty \frac{h_0(c)}{\tau(c)} c^2\, dc = 0$$

If we invert the order of integration in the double integral, then introduce c' as variable of integration by equation (41) and finally invert again this becomes

$$\int_0^\infty \frac{h_0(c)}{\tau(c)} c^2\, dc \left[\frac{1}{2} \int_0^\pi \Pi(\chi) \sin \chi\, d\chi - 1\right] = 0$$

This equation is trivally obeyed because the square bracket vanishes in virtue of the definition of $\Pi(\chi)$. For values of n higher than 0, the integrability condition deduced from (77) is not generally obeyed for any function $h_0(c)$. Such a statement may be proved by examples; these examples will arise in the course of the calculations to follow. Thus we find that except in the passage from $h_0(c)$ to $h_1(c)$, the recursion system is such tbat at each stage it imposes a condition upon the h_r's already determined if the new $h_{n+1}(c)$ is to exist at all. With such an infinity of

conditions one can improve indefinitely an initial trial function assumed for $h_0(c)$.

The integrability conditions whose general structure is thus indicated have actually already been written down. They are the equations (49) for the special case $s = \nu$. Generally speaking, the relations (49) are also of tbe recursion type, permitting us to start with arbitrary averages $\langle c^s \rangle$, and computing successively $\langle c^s P_1 (\cos \vartheta) \rangle$ etc. At every stage, however, there is the exception mentioned: the equation for whicb $s = \nu$ has no third member, and therefore it imposes a condition upon averages already known from the previous equations. We sball refer to this type of equation as a "truncated" relation.

It is reasonable to assume that $1/\tau(c)$ can be developed into a power series in c because it equals the known constant polarization value for $c = 0$. If this can be assumed then each truncated relation $s = \nu$ is equivalent to a unique relation among velocity averages involving $h_0(c)$ only. One obtains this relation by applying to each member in the truncated relation its own recursion formula and repeating this process until ν is brought down to zero. This process will never lead into anotber truncated relation $s' = \nu'$ because at each step s' increases by at least two units with respect to ν'.

In order to test the method for a known case, it will be applied first to tbe case of constant mean free time. This case is adequately described by the theoretical treatment of Section IIB and the Monte Carlo calculation of Section IID. We have seen that the equations (49) reduce in tbis case to the form (51) which dovetails as shown in Fig. 9; this dovetailing leads to explicit values for certain averages as sbown in Fig. 10. A "computational metbod" is only needed wben one tries to get an average outside this selected list. In the present case tbe reduction of the truncated relations to a condition on $h_0(w)$ is particularly simple as is seen from Fig. 9. A singular relation which starts out as between $\langle c^{\nu-1} P_{\nu-1} (\cos \vartheta) \rangle$ and $\langle c^\nu P_\nu (\cos \vartheta) \rangle$ actually yields tbe numerical value of the latter because the former has been obtained numerically in a previous stage. This numerical value yields in combination with previous information $\langle c^{\nu+1} P_{\nu-1} (\cos \vartheta) \rangle$, $\langle c^{\nu+2} P_{\nu-2} (\cos \vartheta) \rangle$ etc and finally $\langle c^{2\nu} \rangle$. Thus we end up with tbe set of even moments of $h_0(c)$ which may be used in succession to determine $h_0(c)$ more and more closely. There is no guarantee that this procedure converges mathematically, since tbe general theorems usually require the knowledge of all integer moments.[20]

[20] Shohat, J. A., and J. D. Tamarkin, The Problem of Moments. Am. Math. Soc., 1943. The original three-dimensional formulation appears a little more favorable for a proof because, in this case, we know indeed all integer moments.

The justification for the method rests therefore on an empirical basis at this point.

Assuming isotropic scattering, as in the "Monte Carlo" calculation we express our results in terms of the dimensionless variable **w** defined in (75). The equation system (51) becomes then

$$\begin{aligned}(2\nu - 1)(1 - \langle I_{s,\nu}(\chi)\rangle)\langle s, \nu\rangle &= \\ = \nu(\nu + s + 1)\langle s - 1, \nu - 1\rangle &+ (\nu + 1)(\nu - s)\langle s - 1, \nu + 1\rangle\end{aligned} \tag{78}$$

where the abbreviation $\langle s, \nu\rangle$ has been introduced for $\langle w^s P_\nu (\cos \vartheta)\rangle$ and the quantities $\langle I_{s,\nu}(\chi)\rangle$ are simple numbers computable from (48b) and the assumption of isotropic scattering. The first truncated relation is $s = \nu = 1$. It yields

$$\langle 1, 1\rangle = 2$$

Reducing it with the relation (78) for which $s = 2$, $\nu = 0$ we get

$$\langle 2, 0\rangle = 8 \tag{79}$$

The next truncated relation is $s = \nu = 2$, which yields

$$\langle 2, 2\rangle = \frac{16}{3}$$

and the reduction gives

$$\begin{aligned}\langle 3, 1\rangle &= \frac{92}{3} \\ \langle 4, 0\rangle &= 184\end{aligned} \tag{80}$$

Similarly in the next stage

$$\begin{aligned}\langle 3, 3\rangle &= \frac{128}{7} \\ \langle 4, 2\rangle &= \frac{18112}{133} \\ \langle 5, 1\rangle &= \frac{421600}{399} \\ \langle 6, 0\rangle &= \frac{3372800}{399}\end{aligned} \tag{81}$$

As an example of an average which cannot be had explicitly we may take the mean absolute value of the speed, that is $\langle 1, 0\rangle$. We find this

value hy picking a sequence of trial functions for $h_0(w)$ with the appropriate number of parameters and imposing successively (79), (80) and (81) upon this sequence; this leads us to a sequence of values for $\langle w \rangle$ which can then he examined. In such a procedure careful consideration of the trial functions is an important element. The following information is availahle. It was proved in Section IID that $h_0(w)$ is logarithmically infinite at the origin. At infinity, on the other hand, $h_0(w)$ falls as e^{-w} times some power of w. One way to check this is to drop the terms containing $1/c$ as factor in (46); the solution of the recursion system becomes then

$$h_\nu(w) \sim (2\nu + 1)e^{-w}w^k$$

where k is some unknown exponent. Armed with this fore-knowledge, we shall use the following sequence of trial function for $h_0(w)$

$$h_0(w) = pEi(w) + qK_0(w) + re^{-w} + swK_1(w) \tag{82}$$

where

$$Ei(w) = \int_w^\infty \frac{e^{-u}}{u}\, du$$

and $K_0(w)$, $K_1(w)$ are the modified Hankel functions of order zero and 1.[21]

·We find in zeroth approximation from normalization only

$$p^{(0)} = \frac{3}{2} \qquad q^{(0)} = r^{(0)} = s^{(0)} = 0$$

$$\langle w \rangle^{(0)} = 2.2500 \tag{83a}$$

in first approximation, using (79)

$$p^{(1)} = \frac{5}{6}$$

$$q^{(1)} = \frac{4}{9} \qquad r^{(1)} = s^{(1)} = 0$$

$$\langle w \rangle^{(1)} = 2.3818 \tag{83b}$$

[21] This definition, which is in accord with the tables of Jahnke-Emde, differs from the usual one by a factor $2/\pi$. This change is suggested by Watson, Bessel Functions, p. 79, and proves convenient in the following.

in second approximation, using (79) and (80)

$$p^{(2)} = \frac{7}{12}$$

$$q^{(2)} = \frac{32}{45} \qquad s^{(2)} = 0$$

$$r^{(2)} = -\frac{1}{20}$$

$$\langle w \rangle^{(2)} = 2.3858 \tag{83c}$$

and in third approximation, using (79), and (80) and (81)

$$p^{(3)} = \frac{3079}{7980}$$

$$q^{(3)} = \frac{202544}{209475}$$

$$r^{(3)} = -\frac{2507}{18620}$$

$$s^{(3)} = \frac{3152}{209475}$$

$$\langle w \rangle^{3} = 2.3864 \tag{83d}$$

Appearances indicate strongly that the sequence (83) for $\langle w \rangle$ approaches a limit which one would guess to be

$$\langle w \rangle = 2.3865 \tag{84}$$

More evidence that the conclusion drawn is correct can be obtained by using the set of trial functions

$$h_0(w) = pK_0(w) + qe^{-w} + rwe^{-w}$$

We find then the following sequence of values for $\langle w \rangle$.

$$\langle w \rangle^{(0)} = 2.546 \qquad \langle w \rangle^{(1)} = 2.395 \qquad \langle w \rangle^{(2)} = 2.388$$

This descending sequence confirms (84) by approaching this same value from above.

Further evidence for the correctness of the procedure can be obtained by deriving a function $h_0(w)$ from the Monte Carlo function $h(\mathrm{w})$ discussed in Section IID and comparing it with our trial function. The function was constructed by covering Fig. 13 with a grid of concentric

circles and horizontal lines and replacing the integration

$$h_0(w) = 2\pi \int_{\vartheta=0}^{\vartheta=\pi} h(\mathrm{w})\, d\,(\cos\vartheta)$$

by a summation over grid points. The function $h_0^+(w)$ so obtained is compared in Table I with $h_0^{(0)}(w)$, $h_0^{(1)}(w)$ and $h_0^{(2)}(w)$ as defined by (82) and the numbers following. We observe that the first approximation

TABLE I

Comparison of the Monte Carlo $h_0^+(w)$ for $h_0(w)$ with successive approximations obtained by the new method.

w	$h_0^+(w)$	$h_0^{(0)}(w)$	$h_0^{(1)}(w)$	$h_0^{(2)}(w)$
0		∞	∞	∞
0.5	0.74	0.8397	0.7281	0.7144
1	0.29	0.3291	0.3019	0.3002
1.5	0.15	0.1500	0.1438	0.1440
2	0.081	0.0734	0.0730	0.0733
2.5	0.0412	0.0374	0.0384	0.0387
3	0.0199	0.0196	0.0207	0.0208
3.5	0.0118	0.0105	0.0114	0.0114
4	0.0063	0.0057	0.0063	0.0063
4.5	0.0030	0.0031	0.0035	0.0036
5	0.0014	0.0017	0.0020	0.0020
6	0.0004	0.0005	0.0007	0.0006
7	0.0001	0.0002	0.0002	0.0002

is an improvement over the zeroth one, while the second one makes little difference, considering the accuracy to which $h_0^+(w)$ is given. In individual cases the sequence drifts away from $h_0^+(w)$; this is not surprising because the latter function is very rough; this is to be expected from its mode of derivation.

The application of this method to the hard sphere model of ion-atom collisions offers no new feature of principle. The actual working out of results is somewhat more complicated, mainly because the connection diagram for the recursion system (49) is more involved. According to equation (26b) the dimensionless variable to be used in this work is

$$\mathrm{w} = \frac{\mathrm{c}}{\sqrt{a\lambda}} \tag{85}$$

We denote its averages $\langle w^s P_\nu\,(\cos\vartheta)\rangle$ by $\langle s, \nu\rangle$ as previously. The equa-

tion system (49) then takes the form

$$(2\nu + 1)(1 - \langle I_{s,\nu}(\chi)\rangle)\langle s + 1, \nu\rangle = \\ = \nu(\nu + s + 1)\langle s - 1, \nu - 1\rangle + (\nu + 1)(s - \nu)\langle s - 1, \nu + 1\rangle \tag{86}$$

The numbers $\langle I_{s,\nu}(\chi)\rangle$ were already discussed in connection with the system (78). What distinguishes (86) from (78) is the way in which the variables are connected; the new connection diagram which replaces Fig. 9 is shown in Fig. 14. The truncated relations no longer dovetail into each other as they did before. Only the first stage proceeds in a similar way, yielding explicit expressions for $\langle 2, 1\rangle$ and $\langle 4, 0\rangle$. In the next stage we

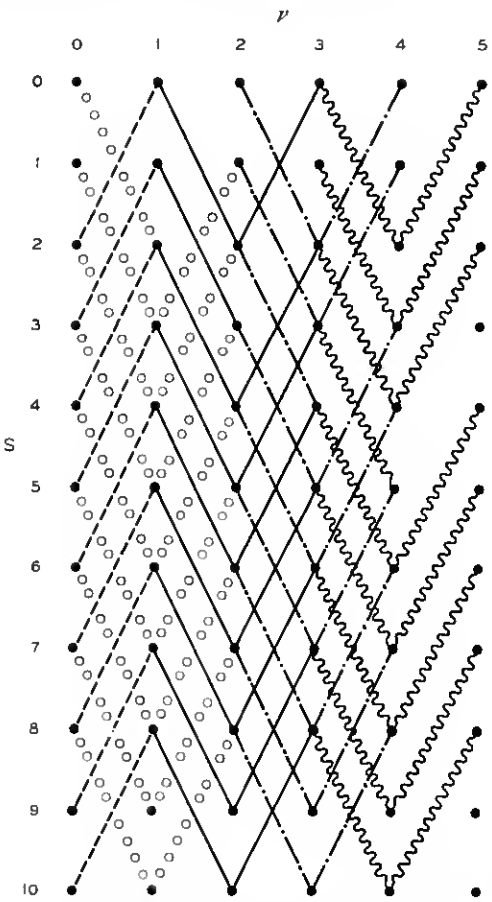

Fig. 14 — Interconnection established by the Boltzmann equation among the averages $\langle c^s P_\nu(\cos\vartheta)\rangle$; case of constant mean free path.

start out with a relation between $\langle 1, 1\rangle$ and $\langle 3, 2\rangle$. By the use of regular recursion formulas we can suceessively transform this into a relation between $\langle 3, 0\rangle$ and $\langle 3, 2\rangle$, then $\langle 3, 0\rangle$ and $\langle 5, 1\rangle$ and finally between $\langle 3, 0\rangle$ and $\langle 7, 0\rangle$. Here we have for the first time the normal situation in which we do not get the actual value of a moment of $h_0(c)$ but only a relation between two or more of such moments; the reason for this is that the system fails to connect up with $\langle 0, 0\rangle$ which equals unity a priori. A similar situation prevails for the next truncated relation; it is originally a relation between $\langle 2, 2\rangle$ and $\langle 4, 3\rangle$ and is finally reduced to one between $\langle 2, 0\rangle$, $\langle 6, 0\rangle$ and $\langle 10, 0\rangle$. Similarly, the next truncated relation reduces to a relation between $\langle 5, 0\rangle$, $\langle 9, 0\rangle$ and $\langle 13, 0\rangle$ and so forth. The first three of these redueed relations come out to be

$$\langle w^4\rangle = 10 \tag{87}$$

$$3\langle w^7\rangle = 112\langle w^3\rangle \tag{88}$$

$$\frac{295}{56}\langle w^6\rangle = 27\langle w^2\rangle + \frac{17}{330}\langle w^{10}\rangle \tag{89}$$

These formulas will now be imposed upon a sequence of trial functions for $h_0(w)$ suitably chosen. Again, we may make use of the information of Section IID, according to which $h_0(w)$ is logarithmically singular at the origin. For large w we proceed as previously from (46) leaving off the terms of $1/c$. We get then

$$h_\nu(w) \sim (2\nu + 1)e^{-\frac{1}{4}w^2}w^k$$

This suggests the following trial function for $h_0(w)$

$$h_0(w) = pEi(\tfrac{1}{2}w^2) + qK_0(\tfrac{1}{2}w^2) + re^{-\frac{1}{4}w^2} + sw^2K_1(\tfrac{1}{2}w^2) \tag{90}$$

The best zero order approximation is actually obtained by the function $K_0(\frac{1}{2}w^2)$. We find

$$q^{(0)} = \frac{\pi}{2\Gamma^2(\frac{3}{4})} = 1.04605 \qquad p^{(0)} = r^{(0)} = s^{(0)} = 0$$

In first order we get, using (87)

$$p^{(1)} = -0.46543 \qquad r^{(1)} = s^{(1)} = 0$$
$$q^{(1)} = 1.45285$$

In the second order, using (87) and (88)

$$p^{(2)} = -0.80856$$
$$q^{(2)} = 1.88127 \qquad s^{(2)} = 0$$
$$r^{(2)} = -0.09804$$

In third order, using (87) and (88) and (89)

$$p^{(3)} = -1.15071$$
$$q^{(3)} = 2.37034$$
$$s^{(3)} = 0.02062$$
$$r^{(3)} = -0.29016$$

These successive approximations lead to tbe following sequence for the drift velocity $\langle w \cos \vartheta \rangle$

$$\langle w \cos \vartheta \rangle^{(0)} = 1.04605 \tag{91a}$$
$$\langle w \cos \vartheta \rangle^{(1)} = 1.14256 \tag{91b}$$
$$\langle w \cos \vartheta \rangle^{(2)} = 1.14616 \tag{91c}$$
$$\langle w \cos \vartheta \rangle^{(3)} = 1.14661 \tag{91d}$$

We conclude from this sequence that

$$\langle w \cos \vartheta \rangle = 1.1467 \tag{92}$$

In addition to the drift velocity there is some interest in the energy and the energy partition. For the energy the following numbers are obtained

$$\langle w^2 \rangle^{(0)} = 2.1884 \tag{93a}$$
$$\langle w^2 \rangle^{(1)} = 2.3395 \tag{93b}$$
$$\langle w^2 \rangle^{(2)} = 2.3511 \tag{93c}$$
$$\langle w^2 \rangle^{(3)} = 2.3531 \tag{93d}$$

giving

$$\langle w^2 \rangle = 2.353 \tag{94}$$

A zero order value for $\langle w^2 \cos^2 \vartheta \rangle$ cannot be said to exist because the first truncated relation is the condition that a distribution function $h_2(w)$ exists at all. Thus, we can get only three numbers in a scquence approximating $\langle w^2 \cos^2 \vartheta \rangle$

$$\langle w^2 \cos^2 \vartheta \rangle^{(1)} = 1.8005 \tag{95a}$$
$$\langle w^2 \cos^2 \vartheta \rangle^{(2)} = 1.7696 \tag{95b}$$
$$\langle w^2 \cos^2 \vartheta \rangle^{(3)} = 1.7685 \tag{95c}$$

giving

$$\langle w^2 \cos^2 \vartheta \rangle = 1.768 \tag{96}$$

We can understand the results (92), (94) and (96) by giving the fraction of the total energy in ordered motion and the fraction of the energy in motion along the z-direction. We find for the first ratio

$$\frac{\langle w \cos \vartheta \rangle^2}{\langle w^2 \rangle} = 0.559 \tag{97}$$

and for the second

$$\frac{\langle w^2 \cos^2 \vartheta \rangle}{\langle w^2 \rangle} = 0.751 \tag{98}$$

The ratio (97) equals 0.5000 for all mean free time models; the ratio (98) is 0.778 for the mean free time model with isotropic scattering. Thus, the deviations from the earlier results are not drastic. However, in certain derived relations the difference is more noticeable. For instance, a good measure of the anistropy of the diffusion process is furnished by the ratio of the random energy along the field to the energy at right angles.[22] From (97) and (98) we find for this number

$$\frac{\langle w^2 \cos^2 \vartheta \rangle - \langle w \cos \vartheta \rangle^2}{\frac{1}{2}(\langle w^2 \rangle - \langle w^2 \cos^2 \vartheta \rangle)} = 1.54 \tag{99}$$

For the mean free time ease this number equals 2.50. Hershey[6] in his work assumes this number to be 1.000.

A comprehensive list of velocity averages is attached in Table II. As a comment I may add that the obvious mode of constructing such a table, namely hy computing the column $\nu = 0$ from (90) and then using the recursion system (86) for the others, runs into some difficulty. First of all, a series of cancellations reduces the accuraey as ν increases; finally, at the positions marked "impossible" we find the missing third members of the truncated relations. These elements cannot be eomputed hy recursion at all, but would require an explicit solution of the equation system (47) for $h_{\nu+1}(c)$. In the table, this more arduous path is not followed. Instead, the recursion method is used for the numbers in italic type and a few numbers are added by extrapolation. The numhers so obtained will be needed in Section IVB.

The calculations on the hard sphere model are immediately applieable to the experimental data of Figs. 3 to 7, which exhibit the drift velocity of

[22] See below, equations (147) and (165).

the noble gas ions in the parent gas as functions of the parameter a/N. These data have a high field range in which the drift velocity varies as the square root of a/N. This is the variation for a model with constant mean free path, as seen from the dimensional formula (26b). It was indicated furthermore in the Section IA that we have good reason to think of the scattering between an ion and an atom as nearly isotropic.[23] These two features characterize uniquely the hard sphere model whose treatment we have just completed. To the extent that they are verified

TABLE II

Dimensionless high-field velocity averages $\langle s, \nu \rangle$ for the hard sphere model and mass ratio unity.

ν	0	1	2	3	4
s					
0	*1.0000*	0.7845	impossible		
1	*1.3923*	*1.1467*	*0.8022*	impossible	
2	*2.3534*	*2.0000*	*1.4759*	0.990	impossible
3	*4.5868*	*3.9853*	*3.0578*	2.134	
4	*10.0000*	*8.8353*	*6.992*	*5.0602*	3.474
5	*23.912*	*21.405*	17.330	12.84	
6	*61.847*	*55.97*	*46.177*	35.36	
7	*171.241*	*156.3*	130.91		
8	*503.7*	*462.81*			
9	*1563*	1445			
10	*5090.9*	4750			

the model is applicable to the experimental data. The formula to apply is (92) in combination with (85):

$$\langle c_z \rangle = 1.147 \sqrt{\frac{a}{N\sigma}} \tag{100}$$

In the logarithmic plot of $\langle c_z \rangle$ vs a/N the intercept of the straight line of slope 1/2 which fits the high field data thus equals

$$\log \frac{1.147}{\sqrt{\sigma}}.$$

The values for σ which result from this are shown in Table III. For comparison are shown the corresponding atomic cross section as determined from viscosity data.[24] It is interesting to observe that the ratio of

[23] A quantitative discussion of this point for the polarization force will follow in Section IIIB.

[24] Landolt-Börnstein, 1950 edition, Vol. I, part 1, page 325.

the two retains very nearly the constant value 3 throughout the table. The fact that the ratio is substantially larger than unity is explained by the resonance feature of the ion-atom scattering process as discussed in Section IA. The fact that it is constant is perhaps an indication of the fact that both processes are governed by overlap conditions of essentially the same wave functions.

I would like to point out in connection with the calculations of this section that the method developed is potentially of very wide application. One question that comes up, for instance, is whether a careful kinetics calculation is necessarily restricted to certain models or whether an ion-atom cross section known numerically could be used to derive therefrom kinetic properties. This is indeed possible. Suppose, for instance, that the cross section $\sigma(c)$ were available as a function of c for collision of He^+-ions and He-atoms and suppose that this cross section were to satisfy the condition of isotropy $\Pi(\chi) = 1$ to a good approxi-

TABLE III

Cross sections for ion-atom and atom-atom collisions for the noble gases.

Gas	ion-atom cross section $\times 10^{16}$ cm^2	atom-atom cross section $\times 10^{16}$ cm^2
He	54	15.0
Ne	65	21.0
A	134	42.0
Kr	157	49
Xe	192	67

mation; we may then derive for this eventuality conditions on $h_0(c)$ which are more general, respectively, than (79) or (87), (80) or (88), (81) or (89). Since we are outrunning here the experimental evidence we shall limit ourselves to the derivation of the first of these relations. The first truncated relation is exactly (50a) which, for isotropy and equal masses, reads

$$\left\langle \frac{c_z}{a\tau(c)} \right\rangle = 2 \tag{101}$$

The reduction of this formula to a condition on $h_0(c)$ requires the relationship $\nu = 0$ of the set (46). This relation is always integrable to yield $h_1(c)$ in terms of $h_0(c)$, as was pointed out early in this section. For the special circumstances assumed the integrated equation is equation (74)

$$h_1(c) = 3 \int_c^\infty \frac{h_0(\gamma)}{a\tau(\gamma)}\, d\gamma \tag{102}$$

The elimination of $h_1(c)$ is achieved by forming the average (101) on the function (102). This leaves the required condition on $h_0(c)$; it may be given the following form

$$\left\langle \frac{\sigma(c)}{c} \int_0^c \gamma^4 \sigma(\gamma)\, d\gamma \right\rangle = 2\,\frac{a^2}{N^2} \tag{103}$$

The equations (79) and (87) are manifestly special cases of this more general relation. Adaptations of this procedure to other cases are clearly possible whenever the need arises.

The calculations of this section are meant to suggest that it is possible to compute reliably average values from a Boltzmann equation without solving it completely. The method employed here for this purpose resembles a Ritz method in that it works with trial functions which must be guessed at, and like that method it is capable of indefinite improvement. The numerical results suggest strongly that we are converging toward a definite answer; however, a mathematical proof of this fact has not been presented. The method will be applied once more in the section on diffusion.

Part III — Motion of Uniform Ion Streams in Intermediate Fields

IIIA. A convolution theorem

Whenever we deal with the motion of a given type of charged particle in a gas of given composition, then there exists a wide range of densities n and N as discussed in Section IA in which the motion of these particles depends only on a/N and kT. For this range the motion is governed by equation (13). Since deriving that equation, all our efforts were dealing with the "high field" equation (34) or (40), in which the gas temperature is taken to be zero and the electric field often scales out, as in (26), (75) and (85). The accomplished solution of this restricted problem, together with the low field solutions available in the literature, brings us back to the more general equation (13) and the question what can be done with it. The topic of Part III so defined is definitely inferior in importance to the one in Part II. For we are studying here an intermediate range of variables which can be handled qualitatively, both in concept and practice, by some sort of interpolation between the high and low field regimes. For precise measurements, conditions can always be chosen so as to satisfy one or the other of the two extremes. For this reason the intermediate field case will only be pushed as far as it will go conveniently, without appeal to numerical methods.

In this Section IIIA we shall give a complete solution of the inter-

mediate field problem for the mean free time models discussed in Section IIB. This solution is achieved by the following theorem: *Given the general equation (13) for constant mean free time*

$$a_T \frac{\partial f(\mathbf{c})}{\partial c_z} + f(\mathbf{c}) = \frac{1}{4\pi} \iint M(\mathbf{C}') f(\mathbf{c}') \Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} \tag{104}$$

and the "high field" equation derived from it by setting the gas temperature equal zero

$$a_T \frac{\partial h(\mathbf{c})}{\partial c_z} + h(\mathbf{c}) = \frac{1}{4\pi} \iint \delta(\mathbf{C}') h(\mathbf{c}') \Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} \cdot \tag{105}$$

and the Maxwellian equation derived from (104) by dropping the field term

$$m(\mathbf{c}) = \frac{1}{4\pi} \iint M(\mathbf{C}') m(\mathbf{c}') \Pi(\chi)\, d\Omega_{\gamma'}\, d\mathbf{C} \tag{106}$$

then the solution $f(\mathbf{c})$ of (104) is the convolution of the solution $h(\mathbf{c})$ of (105) and the solution $m(\mathbf{c})$ of (106):

$$f(\mathbf{c}) = \int h(\mathbf{u}) m(\mathbf{c} - \mathbf{u})\, d\mathbf{u} \tag{107}$$

We carry through the proof by constructing explicitly the equation satisfied by the convolution. We replace the running variables $\mathbf{c}$, $\mathbf{c}'$, $\mathbf{C}$, $\mathbf{C}'$ in (105) by $\mathbf{u}$, $\mathbf{u}'$, $\mathbf{U}$, $\mathbf{U}'$ and multiply in $m(\mathbf{c} - \mathbf{u})$. We get

$$a_T \frac{\partial h(\mathbf{u})}{\partial u_z} m(\mathbf{c} - \mathbf{u}) + h(\mathbf{u}) m(\mathbf{c} - \mathbf{u}) = \\ = \frac{1}{4\pi} \iint \delta(\mathbf{U}') h(\mathbf{u}') m(\mathbf{c} - \mathbf{u}) \Pi(\chi_u)\, d\Omega_{\eta'}\, d\mathbf{U}$$

We now *define* $f(\mathbf{c})$ by the relation (107), and integrate the above equation over $\mathbf{u}$. The second member on the left comes out to be $f(\mathbf{c})$. For the first member, we carry out an integration by parts:

$$\begin{aligned} \int \frac{\partial h(\mathbf{u})}{\partial u_z} m(\mathbf{c} - \mathbf{u})\, d\mathbf{u} &= -\int h(\mathbf{u}) \frac{\partial m(\mathbf{c} - \mathbf{u})}{\partial u_z}\, d\mathbf{u} \\ &= +\int h(\mathbf{u}) \frac{\partial (m(\mathbf{c} - \mathbf{u}))}{\partial c_z}\, d\mathbf{u} \\ &= \frac{\partial}{\partial c_z} \int h(\mathbf{u}) m(\mathbf{c} - \mathbf{u})\, d\mathbf{u} \\ &= \frac{\partial f(\mathbf{c})}{\partial c_z} \end{aligned}$$

For the right hand member we observe that we have the eightfold integration

$$d\Omega_{\eta'}\, d\mathbf{U}\, d\mathbf{u},$$

that is an integration over the collision angles and all final velocity components. By a general principle of kinetic theory[25] we can invert in this integration the final and the initial quantities and write

$$d\Omega_{\eta'}\, d\mathbf{U}\, d\mathbf{u} = d\Omega_{\eta}\, d\mathbf{U}'\, d\mathbf{u}' \tag{108}$$

This puts us in a position to eliminate tbe δ-function by integration. We find

$$a\tau \frac{\partial f(\mathbf{c})}{\partial c_z} + f(\mathbf{c}) = \frac{1}{4\pi} \iint h(\mathbf{u}')m(\mathbf{c} - \mathbf{u})\Pi(\chi_u)\, d\Omega_{\eta}\, d\mathbf{u}' \tag{109}$$

with the side condition that $\mathbf{u}$, $\mathbf{U}$, $\mathbf{u}'$, $\mathbf{U}'$ form a quadruple of vectors in the sense discussed in Section IB for which in addition

$$\mathbf{U}' = 0$$

If we substitute (107) into (104), denoting the dummy variable by $\mathbf{u}'$ instead of $\mathbf{u}$, then tbe two equations (104) and (109) take on a very similar look. A proof of their identity hinges upon proving the identity of the integral terms:

$$\int h(\mathbf{u}')\, d\mathbf{u}' \int m(\mathbf{c} - \mathbf{u})\Pi(\chi_u)\, d\Omega_{\eta} = \int h(\mathbf{u}')\, d\mathbf{u}' \iint M(\mathbf{C}')m(\mathbf{c}' - \mathbf{u}')\Pi(\chi_c)\, d\Omega_{\gamma'}\, d\mathbf{C} \tag{110}$$

The form of tbis relation suggests the assumption that the expressions are identical before integration over $\mathbf{u}'$; this assumption is proved by the events below. The complicated function $h(\mathbf{u}')$ thus disappears from the problem. The other such function, namely $\Pi(\chi)$ disappears then also; for it is by assumption arbitrary, hence could be replaced by a δ-function for a fixed, but arbitrary χ. The two sides of (110) must therefore be equal before we integrate over χ_u or χ_c, and the two χ's are to be taken equal and fixed. Defining angles as shown in the spherical diagram Fig. 15 we thus get (110) in the form

$$\int m(\mathbf{c} - \mathbf{u})\, d\epsilon = \iint M(\mathbf{C}')m(\mathbf{c}' - \mathbf{u}')\, d\phi\, d\mathbf{C} \tag{111a}$$

[25] See Reference 4, Section 3.52.

This is to be true with the side conditions

$$\mathbf{c} = \text{fixed} \tag{111b}$$

$$\mathbf{u}' = \text{fixed} \tag{111c}$$

$$\mathbf{U}' = 0 \tag{111d}$$

$$\chi_c = \chi_u = \chi = \text{fixed} \tag{111e}$$

Equation (111) is an identity involving only elementary functions. Thus the relation itself is in a sense elementary. Those who wish to believe it, may consider the theorem proved; for completeness, however, the proof of (111) will now follow.

Call the left side of (111a) X, the right side Y. To determine X, we substitute from (7) and (111d)

$$\mathbf{u} = \frac{m}{M + m}\,\mathbf{u}' + \frac{M}{M + m}\,\eta$$

with

$$\eta^2 = u'^2$$

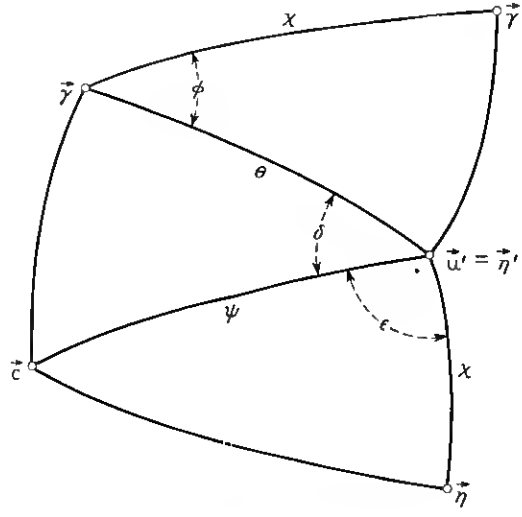

Fig. 15 — Definition of the angles occurring in the proof of the convolution theorem.

because of (9). This yields with the angles as shown on Fig. 15

$$X = \int_0^{2\pi} m(\mathbf{c} - \mathbf{u})\, d\epsilon = \left(\frac{\beta m}{\pi}\right)^{3/2} \exp\left[- \beta mc^2 \right.$$

$$\left. - \beta mu'^2 \frac{M^2 + m^2 + 2Mm\cos\chi}{(M+m)^2} + 2\beta mcu' \frac{m + M\cos\chi}{M+m}\cos\psi \right]$$

$$\cdot \int_0^{2\pi} \exp\left[2\beta \frac{mM}{M+m} cu' \sin\chi \sin\psi \cos\epsilon \right] d\epsilon$$

The integral is evaluated by a formula known from the theory of Bessel functions

$$\int_0^{2\pi} e^{z\cos\epsilon}\, d\epsilon = 2\pi I_0(z) \tag{112}$$

and yields

$$X = \frac{2}{\sqrt{\pi}} (\beta m)^{3/2} \exp\left[- \beta mc^2 - \beta mu'^2 \frac{M^2 + m^2 + 2Mm\cos\chi}{(M+m)^2} \right.$$

$$\left. + 2\beta mcu' \frac{m + M\cos\chi}{M+m}\cos\psi \right] \cdot I_0\left(\frac{2\beta Mm}{M+m} cu' \sin\chi \sin\psi \right) \tag{113}$$

Passing now to the right hand side of (111a) we may replace in the first place $d\mathbf{C}$ by $d\boldsymbol{\gamma}$, because of (111b). $\mathbf{c}'$ and $\mathbf{C}'$ are then replaced by the expressions

$$\mathbf{c}' = \mathbf{c} - \frac{M}{M+m}\boldsymbol{\gamma} + \frac{M}{M+m}\boldsymbol{\gamma}'$$

$$\mathbf{C}' = \mathbf{c} - \frac{M}{M+m}\boldsymbol{\gamma} - \frac{M}{M+m}\boldsymbol{\gamma}'.$$

With the angles defined in Fig. 15, we thus get for Y

$$Y = \left(\frac{\beta M}{\pi}\right)^{3/2} \left(\frac{\beta m}{\pi}\right)^{3/2} \exp\left[- \beta Mc^2 - \beta m(\mathbf{c} - \mathbf{u}')^2 \right]$$

$$\cdot \iiiint \gamma^2\, d\gamma \sin\theta\, d\theta\, d\delta\, d\phi$$

$$\exp\left[- \beta M\gamma^2 + \beta Mc\gamma (\cos\psi\cos\theta + \sin\psi\sin\theta\cos\delta) \right.$$

$$\left. - 2\beta \frac{mM}{M+m} u'\gamma (\cos\theta - \cos\theta\cos\chi - \sin\theta\sin\chi\cos\phi) \right]$$

Integrations over δ and ϕ again go with (112). Beofore writing down the result we shall pass over to a cylindrical coordinate system defined by

$$\gamma_{||} = \gamma \cos\theta \qquad \gamma_{\perp} = \gamma \sin\theta$$

$$\gamma^2 \, d\gamma \sin\theta \, d\theta = \gamma_{\perp} \, d\gamma_{\perp} \, d\gamma_{\perp}$$

The result of tlre first two integrations then reads

$$Y = \frac{4}{\pi} \beta^3 (Mm)^{3/2} \exp\left[-\beta M c^2 - \beta m(\mathbf{c} - \mathbf{u}')^2\right]$$

$$\int_{-\infty}^{+\infty} d\gamma_{||} \exp\left[-\beta M \gamma_{||}^2 + 2\beta M \gamma_{||}\left(c\cos\psi - \frac{mu'}{M+m}(1-\cos\chi)\right)\right]$$

$$\int_0^{\infty} \gamma_{\perp} \, d\gamma_{\perp} \exp\left[\beta M \gamma_{\perp}^2\right] \cdot I_0(2\beta M c \gamma_{\perp} \sin\psi) \cdot I_0\left(2\beta \frac{Mm}{M+m} u' \gamma_{\perp} \sin\chi\right)$$

The first of these two integrals is elementary, the other is Weber's second exponential integral[26] which equals

$$\int_0^{\infty} \exp(-p^2 t^2) I_0(at) I_0(bt) t \, dt = \frac{1}{2p^2} \exp\left(\frac{a^2+b^2}{4p^2}\right) I_0\left(\frac{ab}{2p^2}\right) \qquad (114)$$

This yields for Y exactly the expression (113). The identity (111) is thus proved, and witb it the convolution theorem.

Tbe tbeorem just proved reduces the velocity distribution for arbitrary field and temperature to two components, one containing the field, but not the tempcrature, the other the temperature but not the field. In each of these components, in turn, the variable parameter scales out; thus tbe general distribution reduces to two basic ones one of which is tbe Maxwellian one: the other is worked out partially in the calculations of the Sections IIC and IID. The special case of heavy ion mass has been published independently by Kihara[27] without any apparent knowledge of this theorem which was available in the literature without complete proof.[1] Kihara's form of the theorem is that heavy ions in a light gas have an off-set Maxwellian distribution, with the gas temperature as parameter if the mean free time condition is obeyed for their collisions. Such a function is indeed the convolution of a Maxwellian distribution and the δ-function discussed in the Sections IIB and IIC.

The general distribution function resulting from (107) cannot be written down explicitly because this goal was never achieved for $h(\mathbf{c})$. However we do find a result which is almost a full substitute for this,

[26] Watson, G. N., *A Treatise on the Theory of Bessel Functions*. Cambridge University Press, Section 13.31, 1922.

[27] Kihara, Taro, Rev. Mod. Phys., **24**, p. 45, 1952.

namely that all averages of products of integer powers of tbe Cartesian velocity components, which were shown to be computable in the high field case, can be computed for the intermediate and low field range as well. The calculation proceeds as follows. Suppose we wish to compute the velocity average

$$\langle c_x^m c_y^n c_z^p \rangle = \int c_x^m c_y^n c_z^p f(\mathbf{c})\, d\mathbf{c} \tag{115}$$

for m, n, p integer or zero. We apply the convolution theorem (107) to $f(\mathbf{c})$, decompose the three factors into

$$c_x^m = \{u_x + (c_x - u_x)\}^m$$
$$c_y^n = \{u_y + (c_y - u_y)\}^n$$
$$c_z^p = \{u_z + (c_z - u_z)\}^p$$

and expand each of them by the binomial theorem. We find

$$\langle c_x^m c_y^n c_z^p \rangle = \sum_{\mu=0}^{m} \sum_{\nu=0}^{n} \sum_{\pi=0}^{p} \binom{\mu}{m} \binom{\nu}{n} \binom{\pi}{p} \tag{116}$$
$$\int h(\mathbf{u})\, u_x^{\mu} u_y^{\nu} u_z^{\pi}\, d\mathbf{u} \int m(\mathbf{v}) v_x^{m-\mu} v_y^{n-\nu} v_z^{p-\pi}\, d\mathbf{v}$$

The second integral is a thermal average, the first a high field average computable by the method of Section IIB. Thus the average (116) is a finite sum of products of computable averages and is itself computable.

When formula (116) is applied to the averages (52), (53), (54), (57) and (59) very simple results are found because of the symmetry of the function $m(\mathbf{v})$. For the drift velocity $\langle c_z \rangle$ we get from (52)

$$\langle c_z \rangle = \frac{M + m}{M} \Big/ \left\langle \frac{1 - \cos \chi}{a\tau} \right\rangle \tag{117}$$

This is the same formula as (52) which is tbus proved to bold independently of the gas temperature. In the energy formulas we find simple addition of the thermal and high field values because the middle term in (116) drops out by symmetry. Inserting (53), (54), (57) and (59) we find

$$\langle mc^2 \rangle = 3kT + \frac{(M + m)^3}{M^2} \Big/ \left\langle \frac{1 - \cos \chi}{a\tau} \right\rangle^2 \tag{118}$$

$$\langle mc_z^2 \rangle = kT + \frac{(M + m)^3 \left\langle \dfrac{M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle}{M^2 \left\langle \dfrac{3M \sin^2 \chi + 4m(1 - \cos \chi)}{a\tau} \right\rangle \left\langle \dfrac{1 - \cos \chi}{a\tau} \right\rangle}, \tag{119}$$

$$\langle mc_z^2 \rangle - m\langle c_z \rangle^2 =$$

$$= kT + \frac{(M+m)^2 \left\langle \frac{M \sin^2 \chi + 2m(1-\cos\chi)^2}{a\tau} \right\rangle}{M \left\langle \frac{3M \sin^2 \chi + 4m(1-\cos\chi)}{a\tau} \right\rangle \left\langle \frac{1-\cos\chi}{a\tau} \right\rangle^2} \tag{120}$$

$$\langle mc_x^2 \rangle = kT + \frac{(M+m)^3 \left\langle \frac{\sin^2 \chi}{a\tau} \right\rangle}{M \left\langle \frac{3M \sin^2 \chi + 4m(1-\cos\chi)}{a\tau} \right\rangle \left\langle \frac{1-\cos\chi}{a\tau} \right\rangle^2} . \tag{121}$$

The interpretation of these formulas is implicit in the discussion of the high field formulas given earlier. In particular the combination of the equations (55) and (116) can be given the elegant form

$$m\langle c^2 \rangle = M\langle C^2 \rangle + m\langle c_z \rangle^2 + M\langle c_z \rangle^2 \tag{122}$$

It states that the energy of an ion is obtained by adding the energy of a gas molecule, the energy visible in the drift motion and a storage term which is M/m times the energy in the drift motion; this term becomes important for electrons in a gas. A low field approximation to this formula (in which the second term on the right may be neglected) has been published in the article of Kihara.[28]

IIIB. RESULTS FOR THE POLARIZATION FORCE AND THE ISOTROPIC "MAXWELLIAN" MODEL

The polarization force between ions and molecules which predominates over other forces at sufficiently low temperature satisfies the mean free time requirement of the preceding section. It follows that the complete theory given for those conditions applies to this force. The magnitude of force was given in (4). Its potential equals

$$V = \frac{1}{2} \frac{e^2 P}{\rho^4} \tag{123}$$

Classical theory is usually applicable to the scattering by the potential (123) because angular momentum quantum numbers run as high as 30 or 50 in normal situations.[29] This classical type theory, first developed by Langevin,[30] follows standard elementary methods for computing the

[28] Reference 27, formula 5.12.

[29] Holstein, Theodore, private communication, see also Reference 11.

[30] Langevin, Ann. de Chim. et de Phys., 5, p. 245, 1905.

angle of deflection χ due to a potential of the type (123). The result is

$$\chi = \pi - 2\int_0^{u_1} \frac{du}{\left\{\frac{1}{b^2} - u^2 + \frac{e^2P(M+m)}{Mmb^2\gamma^2}\,u^4\right\}^{1/2}} \tag{124}$$

Here b is the "impact parameter", and u_1 is the lower of the two positive roots of the polynomial in the denominator; if the polynomial has no real root, the integration goes from 0 to ∞. The question whether the denominator has a real root or not is tied up with the nature of the orbit. If b is sufficiently large a root exists and the orbit looks like a hyperbola, Fig. 2(a); for small b no root exists and the two particles are "sucked" towards each other in a spiralling orbit as shown in Fig. 2(b). The two regimes are separated by a limiting orbit in which the particles spiral asymptotically into a circular orbit. This limiting orbit is found by setting the discriminant of the square root in (124) equal to 0. We find

$$b_{\text{lim}}^4 = \frac{4e^2P(M+m)}{Mm\gamma^2} \tag{125}$$

From this value of b_{lim} a cross section and a mean free time τ_s for spiralling collisions can be derived. We find

$$\tau_s = \frac{1}{2\pi eN}\left\{\frac{Mm}{(M+m)P}\right\}^{1/2} \tag{126}$$

This is indeed a constant mean free time as stated, the speed of encounter γ having dropped out.

$1/\tau$ is the dimensional quantity entering into the averages $\langle\varphi(\chi)/\tau\rangle$ which occur in the Sections IIB and IIIA. In working them out in detail as was done by Hassé[9] one has to take into account hyperbolic collisions also; for them a τ cannot be defined or comes out to be zero in the mean. This is due to small angle deflections which are infinitely probable. However, any quantity $\varphi(\chi)/\tau$ to be averaged in a physical problem contains a $\varphi(\chi)$ which vanishes for such impacts. Hence finite averages result which do not give overdue weight to these types of collisions. Following Hassé[9], we do this in the following way for the present case. We write (124) in the form

$$\chi = \pi - 2\int_0^{v_1} \frac{dv}{\left\{1 - v^2 + \frac{v^4}{4\beta^4}\right\}^{1/2}} \tag{127}$$

Here v equals bu and the parameter β equals b/b_{lim}. It is the parameter β introduced by Hassé. Now by the definition of τ we have

$$\left\langle \frac{\varphi(\chi)}{\tau} \right\rangle = N \int \gamma\varphi(\chi)\, d\sigma(\gamma, \chi)$$

$$= N \int_0^\infty \gamma\varphi(\chi) b\, db \int_0^{2\pi} d\epsilon$$

$$= \pi N \gamma b_{\text{lim}}^2 \int_0^\infty \varphi(\chi)\, d(\beta^2)$$

From (125) and (126) the factor in front of the integral just equals $1/\tau_s$; the integral on the other hand is a computable pure number independent of γ which is obtained by inserting into it the relationship (127) between χ and β. Hence we may write

$$\left\langle \frac{\varphi(\chi)}{\tau} \right\rangle = \frac{1}{\tau_s} \int_0^\infty \varphi(\chi)\, d(\beta)^2 \tag{128}$$

The three equations (126), (127) and (128) completely define the nature of the averages appearing in previous sections. The integral (128) has to be computed by numerical methods. It is seen in the course of the evaluations that it naturally decomposes into two parts. The part for which β varies from 0 to 1 deals with spiralling collisions and exists for any $\varphi(\chi)$. For β between 1 and ∞ we get the contribution of the hyperbolic collisions to the average. This part is only finite if $\varphi(\chi)$ vanishes for small angle deflections.

The averages (52), (53), (54), (57) and (59), as well as (117) to (121) contain numerous averages of the form (128) all of which satisfy the predicted condition $\varphi(0) = 0$. They are obtained by linear combination of two basic types: $\langle (1 - \cos\chi)/\tau \rangle$ and $\langle \sin^2 \chi/\tau \rangle$. The first average is given in Hassé.[9] Separating the parts due to spiralling and hyperbolic collisions we find

$$\int_0^1 (1 - \cos\chi)\, d(\beta^2) = 0.8979$$

$$\int_1^\infty (1 - \cos\chi)\, d(\beta^2) = 0.2073$$

This combines to give

$$\left\langle \frac{1 - \cos\chi}{\tau} \right\rangle = \frac{1}{\tau_s} \cdot 1.1052 \tag{129}$$

The analogous result for $\sin^2 \chi$ was obtained by the computing group of Bell Telephone Laboratories

$$\int_0^1 \sin^2 \chi \, d(\beta^2) = 0.511$$

$$\int_1^\infty \sin^2 \chi \, d(\beta^2) = 0.261$$

which gives

$$\left\langle \frac{\sin^2 \chi}{\tau} \right\rangle = \frac{1}{\tau_s} \cdot 0.772 \tag{130}$$

We may now rewrite the major results of Section IIIA for the polarization force. From equation (117) we get

$$\langle c_z \rangle = \frac{0.9048}{2\pi} \sqrt{\frac{1}{M} + \frac{1}{m}} \frac{E}{N\sqrt{P}} \tag{131}$$

This formula may be found in the literature.[31] What is new about (131) is the realization that it is exact at high as well as low electric field.

The formula for the total energy needs no discussion for a special model; it does not involve the angular distribution law when written in the form (122). Thus we would obtain, for instance, for an ion travelling in the parent gas that its total energy is obtained by doubling its apparent energy observable in the drift and adding to this the thermal energy $\frac{3}{2}kT$.

For the partition of the high field component of the energy in the three coordinate directions we have two formulas, formula (58) partitions the entire field contribution of the kinetic energy, formula (60) only its random component. The first formula gives

$$e_x : e_y : e_z = M : M : (M + 6.73m) \tag{132}$$

Formula (60) gives

$$e_x : e_y : e_z^* = (M + m) : (M + m) : (M + 3.72m) \tag{133}$$

It is convenient to apply the general formulas also to the case of constant mean free time, coupled with the assumption of isotropic scattering. This combination of assumptions represents, strictly speaking, an im-

[31] The formula is equation (3), p. 39 of Reference 2, in the limit $\lambda = 0$; or also the last unnumbered equation on p. 919 of Reference 6.

possibility; for we know of no mechanical force which realizes this arrangement. This model was already taken as the basis of the Monte Carlo calculation in Section IID. It will be seen now that it has a wider significance than one might anticipate. The necessary angular averages are

$$\langle 1 - \cos \chi \rangle = 1 \tag{134}$$

$$\langle \sin^2 \chi \rangle = \tfrac{2}{3} \tag{135}$$

This yields for (117)

$$\langle c_z \rangle = \frac{M + m}{M} a\tau \tag{136}$$

As usual, the formula for the energy does not involve the law of scattering if written in the form (122). If we choose the form (118) instead we get in agreement with (79)

$$\langle mc^2 \rangle = 3kT + \frac{(M+m)^3}{M^2} a^2\tau^2 \tag{137}$$

The partition formula (58) becomes

$$e_x : e_y : e_z = M : M : (M + 6m) \tag{138}$$

the partition formula (60) which counts random energy only becomes

$$e_x : e_y : e_z^* = (M + m) : (M + m) : (M + 4m) \tag{139}$$

Comparison of these expressions with the ones for the polarization force shows that the difference between it and the isotropic model is remarkably small from a kinetic standpoint. We may see this by comparing (132) and (138) or (133) and (139). For the other formulas, we may compare more specifically the polarization results with an isotropic case having its mean free time τ given by

$$\tau = 0.9048\ \tau_s \tag{140}$$

Equation (136) becomes then identical with (131) and because of (122) the same identity persists for the energy formula (137). In the light of this we may say that it is very nearly correct to state that scattering is isotropic for the polarization force. This qualitatively correct fact was repeatedly made use of in the preceding sections of the paper. The reason for it is chiefly the predominant effect of spiralling collisions. Indeed, equation (140) shows that a modification of τ_s by only 10 per cent takes into account the main influence of hyperbolic collisions.

From the discussion in Section IA it may be seen that the results

obtained for the polarization force have a potentially wide field of application when measurements of ion drift are extended to low temperature. In the meantime, the results apply occasionally at room temperature, whenever we deal with a small ion and are not bothered by special scattering mechanisms having large cross section. An example of this are the molecular noble gas ions in the parent gas whose drift velocities were measured by Hornbeck[16, 17] and Varney.[18] Table IV shows the measured mobility at standard gas density measured for these ions, in comparison with a value obtained from equation (131). The field range from which the observed mobility was obtained is intermediate. There is not only good numerical agreement, but the experiments follow the theory also in that there is little variation of the observed value

TABLE IV

Mobilities at standard density of the noble gas molecular ions. Comparison of the experiment with a formula based on the polarization force only.

Gas	$\mu_{obs.}$ $\frac{cm^2}{Volt\ sec}$	μ_{calc} $\frac{cm^2}{Volt\ sec}$
He	18	18.2
Ne	6.5	6.21
A	1.9	2.09
Kr	1.2	1.18
Xe	0.7	0.74

with the field. The discrepancy between the two columns can be used to determine a hard collision cross section which is to be superimposed on the polarization force, as is suggested in the so-called Langevin model.[30]

IIIC. VELOCITY DISTRIBUTION FUNCTION FOR ELECTRONS

We have almost exhausted the results achieved for intermediate field conditions. For the sake of completeness I shall mention shortly the intermediate field distribution function for electrons whose derivation we owe to the ingenuity of Davydov.[32]

The derivation does not differ in principle from the one presented in Section IIC for the electrons in the high field case. The distribution function is first expanded in spherical harmonics. For group theoretical reasons the scattering term in the Boltzmann equation is diagonal in

[32] Davydov, B., Phys. Zeits. Sowjetunion., **8**, p. 59, 1935. See also Reference 4, pp. 349-350.

such a decomposition even in the presence of molecular agitation. Thence a generalized form of (47) may be derived containing essentially the same terms. Finally, all but the first two spherical harmonics are dropped and two equations analogous to (63) and (64) are obtained. In fact, it is found that equation (63) is maintained entirely. An extremely complicated reasoning is required, on the other hand, to find the generalization of (64). The result is

$$f_1(c) = \left\{\frac{3kT}{M}\frac{df_0}{dc} + 3\frac{m}{M}cf_0(c)\right\}\left\langle\frac{1-\cos\chi}{a\tau(c)}\right\rangle \tag{141}$$

Combining (63) and (141) we find

$$\left(\frac{1}{\left\langle\frac{1-\cos\chi}{a\tau(c)}\right\rangle} + \frac{3kT}{M}\right)\frac{df_0}{dc} + 3\frac{m}{M}cf_0 = 0$$

and hence

$$f_0(c) = \exp\left[-m\int_0^c \frac{c\,dc}{\frac{\frac{1}{3}M}{\left\langle\frac{1-\cos\chi}{a\tau(c)}\right\rangle^2} + kT}\right] \tag{142}$$

This is the so-called Davydov distribution which is a generalization containing within itself the Maxwellian distribution as well as the high field distribution (65).

The mean energy and the drift velocity of electrons may be calculated from (63) and (142). They are obtainable from the literature and will not be discussed here any further. Equipartition of the energy exists at all field conditions.

Part IV — Diffusive Motion of Ions

IVA. DIFFUSION FOR MEAN FREE TIME MODELS

It was proved in Section IC that if there are spatial inequalities in the distribution of the charge carriers then a smoothing out process sets in which can be described as diffusion. This derivation of principle can be supplemented for "Maxwellian" molecules by an explicit computation of the two components of the tensor (24), that is an evaluation of the integral (23). We shall do this by following the method of Maxwell[19]

rather than by generalizing the formal procedure of the Sections IIA, IIB and IIIA. Such a generalization would no doubt be possible, but would increase unduly the bulk of this paper. We shall operate therefore directly on equation (20). To get out the integral (23) we multiply the equation vectorially with $\mathbf{c}$ and integrate over $d\mathbf{c}$. This operation makes the first term vanish completely. This is obvious from symmetry for the components c_x and c_y of the multiplier $\mathbf{c}$. For c_z we have

$$a \int \frac{\partial g}{\partial c_z} c_z \, d\mathbf{c}$$

An integration by parts brings this in the form (18) and thus makes it equal to zero.

Temporarily, we may break the integral term of (20) into two parts, using some artificial procedure to eliminate small angle collisions. The first half of the integral term reads then simply

$$\frac{1}{\tau} \int g(c)\mathbf{c} \, d\mathbf{c}$$

This is already the desired average (23). On the second half we use the identity (108) to give it the form

$$-\frac{1}{4\pi\tau} \iint M(\mathbf{C}')g(\mathbf{c}')\mathbf{c}\Pi(\chi) \, d\Omega_\gamma \, d\mathbf{C}' \, d\mathbf{c}'$$

We now use (7) to replace $\mathbf{c}$ by the expression

$$\mathbf{c} = \frac{m}{M+m}\mathbf{c}' + \frac{M}{M+m}\mathbf{C}' + \frac{M}{M+m}\boldsymbol{\gamma}$$

Only $\boldsymbol{\gamma}$ is affected by the integration over $d\Omega_\gamma$ which we take up first. Using $\boldsymbol{\gamma}'$ as the axis of a polar coordinate system we may write

$$\boldsymbol{\gamma} = \boldsymbol{\gamma}_{\parallel} + \boldsymbol{\gamma}_{\perp}$$

For every value of χ, $\boldsymbol{\gamma}_{\parallel}$ has the fixed value $\boldsymbol{\gamma}' \cos\chi$. On the other hand the average of $\boldsymbol{\gamma}_{\perp}$ vanishes through integration over all azimuths. Thence we may write

$$\frac{1}{4\pi}\int \mathbf{c}\Pi(\chi) \, d\Omega_\gamma = \frac{m}{M+m}\mathbf{c}' + \frac{M}{M+m}\mathbf{C}' + \frac{M}{M+m}(\mathbf{c}' - \mathbf{C}')\langle\cos\chi\rangle$$

$$= \frac{m + M\langle\cos\chi\rangle}{M+m}\mathbf{c}' + \frac{M\langle 1 - \cos\chi\rangle}{M+m}\mathbf{C}'$$

We now multiply with $M(\mathbf{C}')g(\mathbf{c}')$ and integrate over $d\mathbf{c}' \, d\mathbf{C}'$. The integration of the term containing $\mathbf{C}'$ obviously vanishes for two independent reasons. The integration of the term in $\mathbf{c}'$, finally, yields again the average

(23). Combining the two pieces, we find

$$\frac{M}{M+m}\left\langle\frac{1-\cos\chi}{\tau}\right\rangle\int g(\mathbf{c})\mathbf{c}\,d\mathbf{c}$$

In this expression, the artificial exclusion of small angle scattering is no longer necessary and can be dropped. Completing the integrating of equation (20) we see that the right hand side gives averages over the unperturbed velocity distribution $f(\mathbf{c})$. Combining pieces, using (23) and indices 1, 2, 3 for the x, y and z components we get

$$\mathbf{j}_i(\mathbf{r},t) = -n(\mathbf{r},t)\sum_{\nu=1}^{3}k_\nu\left[\frac{M+m}{M\left\langle\frac{1-\cos\chi}{\tau}\right\rangle}\{\langle c_ic_\nu\rangle-\langle c_i\rangle\langle c_\nu\rangle\}\right] \tag{143}$$

According to (16) and (24), the square bracket in (143) is the diffusion tensor. It has two distinct components which equal respectively

$$D_{\parallel} = \frac{M+m}{M}\frac{\langle c_z^2\rangle-\langle c_z\rangle^2}{\left\langle\frac{1-\cos\chi}{\tau}\right\rangle} \tag{144}$$

$$D_{\perp} = \frac{M+m}{M}\frac{\langle c_x^2\rangle}{\left\langle\frac{1-\cos\chi}{\tau}\right\rangle} \tag{145}$$

The velocity averages entering are (120), and (121), that is the directional components of the random part of the energy. Substituting we get finally

$$D_{\parallel} = \frac{(M+m)kT}{Mm\left\langle\frac{1-\cos\chi}{\tau}\right\rangle} + a^2\frac{(M+m)^3\left\langle\frac{M\sin^2\chi+2m(1-\cos\chi)^2}{\tau}\right\rangle}{M^2m\left\langle\frac{3M\sin^2\chi+4m(1-\cos\chi)}{\tau}\right\rangle\left\langle\frac{1-\cos\chi}{\tau}\right\rangle^3} \tag{146}$$

$$D_{\perp} = \frac{(M+m)kT}{Mm\left\langle\frac{1-\cos\chi}{\tau}\right\rangle} + a^2\frac{(M+m)^4\left\langle\frac{\sin^2\chi}{\tau}\right\rangle}{M^2m\left\langle\frac{3M\sin^2\chi+4m(1-\cos\chi)}{\tau}\right\rangle\left\langle\frac{1-\cos\chi}{\tau}\right\rangle^3} \tag{147}$$

The diffusion coefficients have the simple property that they are obtained by adding the low field and the high field limiting expressions.

This is a consequence of the limited form of the convolution theorem proved in Section IIIA; it probably implies also that the theorem can be extended in some form to include the case of diffusion.

It has been mentioned in the Section ID that the Nernst-Townsend relation (30) applies only to ions moving in a low field. We are now in a position to examine possible extensions of it to general fields. Equations (144), (145) and (117) suggest the form

$$\frac{D_n}{\text{mobility}} = \frac{2 \times \text{mean random energy along } n}{e} \tag{148}$$

where n stands for one of the principal directions of the diffusion tensor. This formula contains equation (30) as a specialization to the low field case.

Formula (148) is one of the formulas obtained in this study of ion motion in which model parameters do not appear. It is valid (a) for all interactions at low field and (b) for the mean free time case at all fields. It also holds dimensionally at high field for models obeying (25); this may be seen from (26a) and (28a). It appears a reasonable conjecture that (148) is approximately true for any law of interaction; the question will he taken up again in the next section.

Let us, in conclusion, write down the formulas resulting from (146) and (147) for the two special mean free time models studied in detail in Section IIIB: the polarization force and the isotropic model. The necessary averages are (129), (130), (134) and (135). They yield for the polarization force

$$D_{\|} = \frac{M+m}{Mm} 0.905\tau_s \cdot kT + \frac{1}{3}\frac{(M+m)^3(M+3.72m)}{M^2m(M+1.908m)} a^2(0.905\tau_s)^3 \tag{149}$$

$$D_{\perp} = \frac{M+m}{Mm} 0.905\tau_s \cdot kT + \frac{1}{3}\frac{(M+m)^4}{M^2m(M+1.908m)} a^2(0.905\tau_s)^3 \tag{150}$$

and for the case of isotropic scattering

$$D_{\|} = \frac{M+m}{Mm}\tau kT + \frac{1}{3}\frac{(M+m)^3(M+4m)}{M^2m(M+2m)} a^2\tau^3 \tag{151}$$

$$D_{\perp} = \frac{M+m}{Mm}\tau kT + \frac{1}{3}\frac{(M+m)^4}{M^2m(M+2m)} a^2\tau^3 \tag{152}$$

Just as in the earlier study the results for the two models do not differ appreciably.

IVB. LONGITUDINAL DIFFUSION FOR THE HARD SPHERE MODEL

Whenever the mean free time condition for collisions is not fulfilled, then the computation of diffusion coefficients requires a procedure analogous to that of Section IIE. Since this entails some numerical work the calculation was only carried out for a case which was thought to be of experimental interest, namely for longitudinal diffusion of ions in the parent gas. In other words, we are extending the numerical computation at the end of Section IIE to include longitudinal diffusion. The computation to provide us with the undetermined constant of equation (28b) for the special case when m and M are equal; it also offers, incidentally, a good test case for applying the method of Section IIE outside the area for which it was designed originally.

Since the equation is only to be solved in the high field case we may apply to (20) the reduction method of Section IIA. If we introduce also the specialization warranted by the hard sphere model and unit mass ratio then, in analogy to equation (40), we get the following starting equation

$$\frac{\partial g(\mathbf{w})}{\partial w_z} + wg(\mathbf{w}) - \frac{1}{4\pi}\int_0^\pi \frac{w'^4 \sin\chi\, d\chi}{w^3}\int_0^{2\pi} g(\mathbf{w}')\, d\omega = -\lambda k\{w_z - \langle w_z\rangle\}h(\mathbf{w}) \tag{153}$$

Here the dimensionless variable $\mathbf{w}$ defined by (85) has been employed instead of $\mathbf{c}$.

Equation (153) is the fundamental equation of our problem; it is an inhomogeneous version of equation (40). We solve the equation in the same way as we did previously, namely by decomposing $g(\mathbf{w})$ into spherical harmonics and forming moments. In other words we follow step by step the procedure of Section IIA, the only difference being the presence of an inhomogeneous term. We shall not enumerate all these steps again. We shall only note in passing the inhomogeneous form of (47) which is

$$\frac{1}{2}\int_0^\pi \frac{w'^4}{w^3} g_\nu(w')P_\nu(\cos\kappa)\sin\chi\, d\chi - wg_\nu(w) - \frac{\nu}{2\nu-1}\left\{\frac{dg_{\nu-1}}{dw} - \frac{\nu-1}{w}g_{\nu-1}(w)\right\} - \frac{\nu+1}{2\nu+3}\left\{\frac{dg_{\nu+1}}{dw} + \frac{\nu+2}{w}g_{\nu+1}(w)\right\} = \lambda k\left[\frac{\nu}{2\nu-1}wh_{\nu-1}(w) + \frac{\nu+1}{2\nu+3}wh_{\nu+1}(w) - \langle w_z\rangle h_\nu(w)\right]$$

Having introduced moments in the manner described earlier we arrive at the inhomogeneous version of (49) or (86)

$$\begin{aligned}\nu(s+\nu+1)\{s-1,\nu-1\}+(\nu+1)(s-\nu)\{s-1,\nu+1\}\\ -(2\nu+1)(1-\langle I_{s,\nu}\rangle)\{s+1,\nu\}=-(2\nu+1)\langle 1,1\rangle\langle s,\nu\rangle\\ +\nu\langle s+1,\nu-1\rangle+(\nu+1)\langle s+1,\nu+1\rangle\end{aligned}\tag{154}$$

Here the curly brackets $\{s, \nu\}$ are normalized moments over $g(\mathrm{w})$ defined as follows

$$\{s,\nu\}=\frac{1}{k\lambda}\int g(\mathrm{w})w^{s}P_{\nu}(\cos\vartheta)\,d\mathrm{w}\tag{155}$$

The equations (154) show that the quantities $\{s, \nu\}$ are numbers, the variable density gradient nk having been eliminated by the definition (155). The system does permit that arbitrary amounts of the pointed averages be added to the curly ones. This indeterminacy is removed by the supplementary condition (18) which, in the present notation reads

$$\{0,0\}=0\tag{156a}$$

The connectivity of the equation system (154) is the same as that of (86). Hence it will have the same properties as that earlier system. We may, therefore, reduce it in the manner followed previously and get inhomogeneous versions of the equations (87), (88) and (89). They read

$$\{4,0\}=-\frac{5}{3}\langle 4,1\rangle+\frac{5}{3}\langle 1,1\rangle\langle 3,0\rangle.\tag{157a}$$

$$\begin{aligned}112\{3,0\}-3\{7,0\}&=4\langle 7,1\rangle-4\langle 1,1\rangle\langle 6,0\rangle\\ &+\frac{56}{5}\langle 5,0\rangle+\frac{112}{5}\langle 5,2\rangle\\ &-\frac{168}{5}\langle 1,1\rangle\langle 4,1\rangle\\ &-\frac{1344}{25}\langle 3,1\rangle+\frac{1344}{25}\langle 3,3\rangle\\ &+\frac{448}{5}\langle 1,1\rangle\langle 2,0\rangle-\frac{448}{5}\langle 1,1\rangle\langle 2,2\rangle\end{aligned}\tag{158a}$$

$$-\frac{10}{3}\langle 2,0\rangle-\frac{20}{3}\langle 2,0\rangle+10\langle 1,1\rangle^{2}$$

$$
\begin{aligned}
54\{2,0\} - \frac{295}{28}\{6,0\} + \frac{17}{165}\{10,0\} &= -\frac{17}{135}\langle 10,1\rangle + \frac{17}{135}\langle 1,1\rangle\langle 9,0\rangle \\
&- \frac{17}{36}\langle 8,0\rangle - \frac{17}{18}\langle 8,2\rangle + \frac{17}{12}\langle 1,1\rangle\langle 7,1\rangle \\
&+ 6\langle 6,1\rangle - \frac{21}{5}\langle 6,3\rangle - \frac{44}{5}\langle 1,1\rangle\langle 5,0\rangle + 7\langle 1,1\rangle\langle 5,2\rangle \\
&+ \frac{54}{5}\langle 4,0\rangle + \frac{108}{7}\langle 4,2\rangle - \frac{288}{35}\langle 4,4\rangle \\
&- \frac{162}{5}\langle 1,1\rangle\langle 3,1\rangle + \frac{72}{5}\langle 1,1\rangle\langle 3,3\rangle
\end{aligned} \tag{159a}
$$

Tbe pointed averages over the distribution $h(\mathrm{w})$ may be found in Table II. Substituting them we get

$$\{0,0\} = 0 \tag{156b}$$

$$\{4,0\} = -10.494 \tag{157b}$$

$$112\{3,0\} - 3\{7,0\} = 647.8 \tag{158b}$$

$$54\{2,0\} - \frac{295}{28}\{6,0\} + \frac{17}{165}\{10,0\} = -566.4 \tag{159b}$$

The form (90) tbat was assumed for $h_0(w)$ will again be taken for $g_0(w)$ with new undetermined coefficients p, q, r, s and a factor $k\lambda$ evident from (153) or (155):

$$g_0(w) = k\lambda[pEi(\tfrac{1}{2}w^2) + qK_0(\tfrac{1}{2}w^2) + re^{-\frac{1}{2}w^2} + sw^2K_1(\tfrac{1}{2}w^2)] \tag{160}$$

This is a rather poor assumption because the form (90) was adopted for $h_0(w)$ after an extensive study of the properties of the distribution function $h(\mathrm{w})$. For $g(\mathrm{w})$ we know little beyond the fact that it is some kind of distorted p-type function. The $g_0(w)$ derived from this is not likely to resemble $h_0(w)$ very closely. Thus the choice (160) is mainly based on ignorance and convenience; this explains the slower convergence observed here than in (91), (93) and (95). To start with, the zero order is completely lost because (156) yields a zero coefficient. We find in first order, using (156) and (157)

$$p^{(1)} = 4.8842 \qquad q^{(1)} = -4.2689 \qquad r^{(1)} = s^{(1)} = 0$$

in second order, using (156), (157) and (158)

$$p^{(2)} = -10.542$$
$$q^{(2)} = +14.993 \qquad s^{(2)} = 0$$
$$r^{(2)} = -4.408$$

in third order, using (156), (157), (158) and (159)

$$p^{(3)} = -0.8710$$
$$q^{(3)} = +1.1754$$
$$r^{(3)} = +1.0140$$
$$s^{(3)} = -0.5809$$

The longitudinal diffusion coefficient results from these numbers by the use of (23), (24) and (160). With the notation (155) the formula becomes

$$D_{\parallel} = -a^{1/2}\lambda^{3/2}\{1, 1\} \tag{161}$$

The formula (154) yielding $\{1, 1\}$ from $g_0(w)$ is $s = 2$, $\nu = 0$

$$\{1, 1\} = \tfrac{1}{4}\{3, 0\} + \tfrac{1}{2}\langle 3, 1\rangle - \tfrac{1}{2}\langle 1, 1\rangle\langle 2, 0\rangle \tag{162a}$$

or numerically from the Table II

$$\{1, 1\} = \tfrac{1}{4}\{3, 0\} + 0.6433 \tag{162b}$$

The result is

$$\{1, 1\}^{(1)} = -0.3695 \tag{163a}$$
$$\{1, 1\}^{(2)} = -0.2075 \tag{163b}$$
$$\{1, 1\}^{(3)} = -0.2198 \tag{163c}$$

The numbers do not extrapolate too reliably but one would guess that

$$\{1, 1\} = -0.22$$

is essentially correct. Hence we have

$$D_{\parallel} = 0.22a^{1/2}\lambda^{3/2} \tag{164}$$

In order to gain an appreciation of the value obtained it is worthwhile to compare it with the value that would have been predicted from the generalized Nernst-Townsend relation (148). The mobility concept is ambiguous for all but the cases discussed then. It would seem that the appropriate concept here is the differential mobility because comparison

is made between a small density gradient and a small change in the applied field. Thus we would interpret (148) to mean

$$D_{11} \approx \frac{\partial \langle c_z \rangle}{\partial a} [\langle c_z^2 \rangle - \langle c_z \rangle^2] \tag{165a}$$

which, with (85), (92) and (96), becomes

$$D_{11} \approx 0.26 a^{1/2} \lambda^{3/2} \tag{165b}$$

The error of formula (165) is thus 18 per cent, when compared to (164).

Part V — Concluding Observations

The present article is supposed to contain the essentials of a kinetic theory of charged particles moving through a gas in the presence of an intermediate or high electric field. An effort was made to make the theory general, yet many irksome restrictions will become apparent to those who will try to apply it to their particular prohlem. Especially those who have in mind application to electrons will find the article unsatisfactory. It is true that many sections leave the masses variahle; however, the assumption of elastic collisions, which is made throughout, is almost fatal to all hut the most elementary applications. Thus most of the material is slanted for ions. Within this domain, numerous awkward restrictions are still found here. The most important ones are presumahly the restriction to D.C. conditions, the assumption of "low" ion density, and the omission of all magnetic effects. It is my general impression, which I gained from the convolution theorem Section IIIA and which is confirmed by a recent publication[27] that much can be done to remove these three restrictions provided the mean free time assumption is made for collisions. To many the adoption of the mean free time condition will in itself appear an awkward restriction. In a rigorous sense this is true, and calculations are made in this article for the more appropriate hard sphere model when quantitative comparison with experiment is contemplated (equations (100) and (164)). Indications are even given for a treatment which dispenses altogether with the use of models (equation (103)). However, for rapid advance and easy handling, the mean free time assumption does appear essential. It is therefore important to point out that in a wider semiquantitative sense, the use of this model is no harrier to application. In other words, there is in the mean free time formulas information which suggests a wider validity. This is particularly true for equations which do not contain model parameters, such as (55), (56), (122) and (148). Even formulas which

do contain the mean free time yield to judicious treatment. For example, we have the hard sphere formula (100) for the drift velocity of an ion. This formula happens to be limited to the high field case and mass ratio unity. On the other hand we have formula (136) which holds for all fields and all mass ratios, but assumes constant mean free time. We now adopt this formula as a general guess for the hard sphere model, interpreting τ as previously as the mean free time between collisions; this quantity is now no longer a constant, but should be taken as

$$\tau = \frac{\lambda}{\sqrt{\langle c^2 \rangle + \langle C^2 \rangle}} \tag{166}$$

The denominator is the root mean square relative velocity which is familiar from other applications. The interpretation (166) yields a tentative formula for the drift for all mass ratios and for all fields. Specializing to the bigh field case, we may neglect $\langle C^2 \rangle$ in (166) and then substitute for $\langle c^2 \rangle$ from (55). This yields tbe higb field formula

$$\langle c_z \rangle \approx \frac{(M + m)^{1/4} m^{1/4}}{M^{1/2}} (a\lambda)^{1/2} \tag{167}$$

This is indeed a very successful formula. For ions in the parent gas it differs from (100) by only 4 per cent. For electrons it checks tbe result of Druyvesteyn[4] to within 12 per cent. Finally, for heavy ions in a light gas, we find exact agreement with equation (71). As a second specialization we may apply (166) to the low field case. We must then set

$$\langle c^2 \rangle + \langle C^2 \rangle = 3kT \left(\frac{1}{m} + \frac{1}{M} \right)$$

and get from (136) and (166)

$$\langle c_z \rangle = \frac{1}{\sqrt{3}} \left(\frac{1}{m} + \frac{1}{M} \right)^{1/2} \frac{eE\lambda}{\sqrt{kT}} \tag{168}$$

All dimensional factors in this formula are correct. Numerically (168) is somewhat inferior to (167); for the factor differs from the correct one[33] by 20 per cent. Nevertheless, the combination of (136) and (166) gives results which are semiquantitatively correct in all relevant limiting cases. This makes it a reliable interpolation formula for intermediate field conditions; for this case $\langle c^2 \rangle$ would have to be substituted from (122) and the resultant quadratic equation solved for $\langle c_z \rangle$.

From the examples given we may conclude that the mean free time formulas contain in essence information applicable to other types of elastic scattering.

[33] See Reference 2, page 40, second equation.

Part VI — Acknowledgements

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